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HIGH TEMPERATURE MASS SPECTROMETRY

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HIGH TEMPERATURE MASS SPECTROMETRY

James A. Roberts, Jr.
(Ph.D. thesis)

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HIGH TEMPERATURE MASS SPECTROMETRY

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ABSTRACT

Two investigations demonstrating new aspects of the high temperature Knudsen cell mass spectrometer technique have been made.

The intensities of mass spectrometer ion peaks attributable to CeF$_3$(g) and Ce$_2$F$_6$(g) have been measured as functions of temperature for the equilibrium vapor over CeF$_3$(s). These results, plus new measurements of the partial vapor pressures over LaF$_3$(s) cast doubt on an explanation suggested by Skinner and Searcy for their anomalous measured entropies of LaF$_3$(g) dimerization. The possibility, which they suggested, that dimer intensities are underestimated because of masking of the principal dimer peaks by monomer peaks cannot be eliminated, but is rendered less likely by the demonstration that that kind of fragmentation is not important for Al$_2$Cl$_6$(g). Measured temperature dependences of the monomer vapor pressures are in satisfactory agreement with values found in earlier torsion effusion measurements. But evidence is presented that measured dimer temperature dependences are anomalously low because of selective scattering of dimers from the molecular beam outside the effusion cell at high beam pressures.

The data seem best interpreted by use of conventional assumptions to obtain dimer/monomer pressure ratios and use of entropies of dimerization estimated from values measured for other systems. This procedure
leads to -51.5 ± 7 kcal for the enthalpy of dimerization of \( \text{CeF}_3(g) \) and -54.2 ± 7 kcal for the enthalpy of dimerization of \( \text{LaF}_3(g) \) at 1577°K.

Ion intensity, time, temperature data have been used to calculate the congruent vaporization composition as a function of temperature for gallium sesquisulfide \( \text{(Ga}_2\text{S}_3) \) between 1050 and 1370°K. Discontinuities in the congruent composition vs temperature curves found at 1230 ± 5°K and 1295 ± 5°K indicate phase transitions.

The congruent composition remains fairly constant at 60.16 a/o S from 1050 to 1190°K. From 1190 to 1230°K the composition gradually changes to 60.11 a/o S. At 1230 ± 5°K the congruent composition discontinuously jumps to 59.77 a/o S. Between 1230 and 1295°K the composition changes linearly to 59.68 a/o S, then discontinuously jumps to 57.6 a/o S. The composition changes between 1295 and 1370°K to 57.3 a/o S.

Partial pressure vs composition at constant composition curves for the two major vapor species, \( \text{S}_2(g) \) and \( \text{Ga}_2\text{S}(g) \), have also been constructed. An anomaly found when the phase transition at 1230°K is traversed wherein the \( \text{Ga}_2\text{S}(g) \) partial pressure temporarily increases when the temperature is decreased is explained by reference to schematic equilibrium free energy diagrams.

The second law heat of vaporization for the stoichiometric reaction \( \text{Ga}_2\text{S}_3(s) = \text{Ga}_2\text{S}(g) + \text{S}_2(g) \) was calculated for the temperature range 1286 to 1050°K to be 157.3 ± 0.5 kcal/mole of \( \text{Ga}_2\text{S}_3 \).
GENERAL INTRODUCTION

This thesis describes Knudsen cell mass spectrometric investigations of (1) the stabilities of the \( \text{Ce}_2\text{F}_6(\text{g}) \) and \( \text{La}_2\text{F}_6(\text{g}) \) dimer molecules and (2) the congruent vaporization composition of gallium sesquisulfide. Although chemically these are rather unrelated topics, each project demonstrates a new aspect of the mass spectrometric technique in its application to high temperature chemical studies.

The dimer studies reveal a source of systematic error which may be encountered in chemical systems with vapor species of very different partial pressures. The source of error is preferential scattering of the minor species from the beam outside the Knudsen cell.

In the gallium sesquisulfide study, mass spectrometry was used to determine the changes in the congruent vaporizing composition of the solid with temperature. The method, which involves integrating ion intensity vs time data, has previously been used to measure gross changes in composition but not to measure the small changes quantitatively examined here. Curves of partial pressure vs composition at constant temperature were calculated from the data. This method is especially satisfying in that it takes particular advantage of the most sensitive aspects of the Knudsen cell mass spectrometric technique, while at the same time it minimizes the weaknesses.
PART 1

THE STABILITIES OF Ce₂F₆(g) AND La₂F₆(g)
I. INTRODUCTION

The existence of La₂F₆ in the equilibrium vapor of lanthanum fluoride has recently been demonstrated by Skinner and Searcy. They found that the entropy for the reaction La₂F₆(g) = 2LaF₃(g) calculated by conventional analysis of the mass spectrometer data appeared anomalously high when compared with entropies of similar reactions. From analogy with observed fragmentation behavior of gaseous halides that contain two different kinds of metal atoms, they reasoned that their anomalous measured entropy was not real but was a result of extensive fragmentation of the La₂F₆ parent to LaF₂⁺ + LaF₃ + F + e⁻ under electron impact in the ion source of the mass spectrometer. The LaF₂⁺ formed in the above reaction would be masked by the LaF₂⁺ which was produced as the major ion species from LaF₃(g). Calculation of pressures from intensities of the fragment peak, La₂F₆⁺, which was not masked, on the assumption that La₂F₆⁺ is the principal peak, would then lead to an apparent pressure of the dimer that was below its actual pressure.

Skinner and Searcy suggested that their interpretation of the lanthanum fluoride data might be tested by studying the dimer to monomer vapor pressure ratios in cerium fluoride vapor. The additional electron on each cerium atom as compared to lanthanum might give added stability to the dimer molecule and might reduce the tendency of the dimer ion to fragment. Thus the measured Ce₂F₆⁺/CeF₂⁺ intensity ratios could more nearly reflect true relative dimer to monomer pressure ratios. Certainly the possibility that concentrations of polymeric vapor species are sometimes underestimated because their principal ionic fragments are masked
by ions from the monomer deserves more detailed examination. The mass spectrometric study of the gaseous species above CeF₃(s) described in this paper was undertaken with that objective.

The present study has yielded Ce₂F₅⁺ to CeF₂⁺ ion intensity ratios close to the La₂F₅⁺ to LaF₂⁺ ratios, but the ratios for the cerium fluoride ions varies more steeply with temperature. This fact suggests that measurements of the temperature dependence of the very low intensity La₂F₅⁺ and Ce₂F₅⁺ peaks may be subject to greater experimental error than supposed by Skinner and Searcy. Accordingly, we have made additional measurements for La₂F₅⁺ and LaF₂⁺ ions and discuss alternate interpretations of the data for both fluoride systems.
II. EXPERIMENTAL

This study was carried out with the same 60° sector, 1 foot radius, magnetic deflection mass spectrometer used in the previous lanthanum fluoride study.\(^1\) Samples were held in a graphite-lined molybdenum effusion cell which was heated by electron bombardment. Temperatures were measured with a Pt vs Pt 10% Rh thermocouple clamped into a hole in the bottom of the cell. The CeF\(_3\), supplied by Electronic Space Products, Inc., was of a nominal 99.9% purity. Small concentrations of other rare earth elements were the principal spectroscopically identifiable impurities.\(^2\) Spectrographic analyses of samples after a run showed no increase in impurity concentrations. Debye-Scherrer X-ray analysis of the samples showed the proper crystal structure and lattice parameters for CeF\(_3\)(s).\(^3\) No lines that did not fit the CeF\(_3\) hexagonal structure were observed. The lanthanum fluoride was the same material used in the earlier study. To extend the range of pressures that could be measured, orifices of three different sizes were used (see Table I).

Ionizing electrons of 70 eV energy produced shutterable ion peaks. Identification of the masses corresponding to the measured ion peaks was made by use of a calibrated gauss indicator and confirmed by comparing the observed mass spectrums with the published isotopic abundances.\(^4\) At least 20 min. were allowed between measurements to ensure that equilibrium was reached.

The ion peaks CeF\(_2^+\) and Ce\(_2\)F\(_6^+\), which must be produced primarily by the dissociative ionization of CeF\(_3\) and Ce\(_2\)F\(_6\) respectively, were observed. A small fraction of the CeF\(_2^+\) may be produced by dissociative ionization of Ce\(_2\)F\(_6\) but the maximum intensity of CeF\(_2^+\) that would result
from this second process is too low to influence significantly the measured CeF$_2^+$ intensities or temperature dependence in the experimental range.

Calibration experiments were conducted during which the intensity of the ion peak corresponding to CeF$_2^+$ was measured as a function of temperature. Second law heats of vaporization were calculated from the slopes of the log (I$^+T$) vs 1/T (I$^+$ = ion intensity, T = absolute temperature, and I$^+T$ is proportional to pressure) curves. The heat calculated, which essentially equals the total heat of vaporization of the solid in the experimental temperature range since the number of dimers present is too low to substantially affect the total heat, was in only fair agreement with the heat of vaporization of cerium fluoride determined by the torsion effusion method reported by Lim and Searcy. To determine which value should be accepted alternate runs over the same temperature range were made on cerium fluoride monomers and on the lanthanum fluoride for which carefully calibrated torsion effusion measurements had been made by Mar and Searcy.

To obtain Ce$_2$F$_5^+$ intensities relative to CeF$_2^+$ as a function of temperature, the measurements had to be carried to higher temperature than in the calibration experiments because of the low intensity of the dimer. Plots of log (I$^+T$) vs 1/T that were obtained for both monomer and dimer showed downward deviations from linearity that were too large to be caused solely by heat capacity changes (Fig. 1).

The deviation from linearity of the Ce$_2$F$_5^+$ data was greater than for the CeF$_2^+$ data. It was apparent, therefore, that a similar bending of the log (I$^+T$) vs 1/T plots in the high pressure range, if an artifact
of the measurements, might have led Skinner and Searcy to a misinterpretation of their lanthanum fluoride measurements. Because dimer data was necessarily collected over a restricted temperature range where the curvature would be most pronounced, the measured slope of the log \((I^+ T)\) vs \(1/T\) curves for the dimer might well be systematically too low relative to that for the monomer.

Superposition of plots of log \((I^+ T)\) vs \(1/T\) for the CeF\(_2^+\) and Ce\(_2\)F\(_5^+\) on plots for LaF\(_2^+\) and La\(_2\)F\(_6^+\) obtained by Skinner and Searcy showed nearly identical monomer to dimer ratios in each system, but a lower temperature dependence for La\(_2\)F\(_6^+\) than for Ce\(_2\)F\(_5^+\). Accordingly, two runs were made to remeasure the LaF\(_3\) to La\(_2\)F\(_6\) ratios in order to determine if the difference in temperature dependence was a consequence of a systematic error in measurements for one or both metal fluoride systems. The new measurements yielded La\(_2\)F\(_5^+\) temperature variations that are closely similar to those found for Ce\(_2\)F\(_5^+\).
III. RESULTS

Systematic differences were found in the absolute values of the measured heats of vaporization of the monomers between the calibration experiments, the cerium fluoride monomer/dimer ratio experiments, and the lanthanum fluoride monomer/dimer ratio experiments. These differences resulted from slight alterations in the effusion cell heating arrangement made between these three sets of measurements when broken heating filaments were replaced. The differences were probably largely consequences of small changes in temperature gradients in the effusion cells. Temperature gradients are particularly difficult to control in mass spectrometers. In an earlier paper, data for vaporization of monomers of various lanthanide element fluorides are summarized and it is pointed out that the entropies of vaporization calculated from various mass spectrometer studies show suspiciously great deviation from each other. Recently Wesley and DeKock have calculated entropies for several lanthanide metal fluorides from spectroscopic data obtained by matrix isolation and have concurred in the conclusion that the data obtained in the torsion effusion studies are in better agreement with the third law entropies than are the results of the mass spectrometer studies.

The influence of systematic temperature errors in the ratios of pressures of two species measured in the mass spectrometer with nearly identical conditions, however, should be relatively low. We have accepted the pressures measured for LaF₃(g) by the torsion effusion method as most reliable because the temperature scale was verified by measurements of the vapor pressure of tin, and we give equal weight to
the enthalpy of vaporization calculated from direct measurement of 
CeF$_3$(g) vaporization and to that calculated from the differences in 
measured pressure dependences found in alternate mass spectrometer runs 
under nearly identical experimental conditions.

The calibration investigation of the lanthanum and cerium fluoride 
monomers made over the temperature range 1280-1488°K yielded second law 
heats of vaporization of 102.1 ± 0.4 and 102.3 ± 0.4 kcal/mol for 
LaF$_3$(g) and 100.0 ± 0.6 and 100.3 ± 0.5 kcal/mol for CeF$_3$(g). These 
runs give an average value of the heat of vaporization of CeF$_3$ that is 
2.0 kcal/mol less than that of LaF$_3$. The torsion effusion data for 
CeF$_3$ indicate the heat of vaporization of CeF$_3$ to be 5.8 kcal/mol less 
than that of LaF$_3$. We assume that the correct value for the heat of 
sublimation of lanthanum fluoride to LaF$_3$(g) is 99.4 kcal/mol at 1495°K, 
as found by Mar and Searcy, and that the value for CeF$_3$(g) is 3.9 kcal/
mol less, 95.5 kcal/mol.

In our initial evaluation of our data, we noticed curvature of the 
log $I^+T$ vs $1/T$ plots at high temperatures (see Fig. 1). Least squares 
fits of log ($I^+T$) vs $1/T$ were made for the CeF$_3$ monomer using all the 
data points taken during a particular run, then excluding only the point 
taken at the highest temperature, then excluding the two points taken at 
the highest temperatures, etc. The value $\lambda/d = 1.36$, where $\lambda =$ mean free 
path of the CeF$_3$ monomer as calculated from the hard sphere model$^{10}$ and 
d = orifice diameter or width, was selected as the value of $\lambda/d$ above 
which curvature significantly influenced the apparent enthalpies of sub-
limation to the monomer. The temperature dependence of the dimer data 
present a special problem which we analyze in the discussion section.
Data judged as acceptable using the above procedure are referred to as "selected" data and are the only data used in thermodynamic evaluations unless it is specifically stated that all data are being considered. The temperature limits for the lanthanum fluoride data were selected using the same λ/d value calculated above and the vapor pressure of LaF₃(g) reported by Mar and Searcy.

To convert the I⁺T data for each monomer to vapor pressures, the least squares fits of the heat capacity-corrected selected data for the monomer for each run were made to coincide with the vapor pressure found at the mid point of torsion-effusion experimental range. The same factors for each run, after corrections for estimated relative cross section for electron impact ionization and isotopic abundance, were applied to the dimer data. The cross section for electron impact ionization of the dimers was estimated to be 1.5 times the cross section for the respective monomers. This is the approximate average found for alkali halide dimers by Berkowitz, et al.¹¹ and is the value used by Skinner and Searcy¹ in their investigation of lanthanum fluoride. The electron multiplier gain was estimated to be the same for both the monomer and dimer.

Fragmentation patterns for both systems and the appearance potentials of the various cerium fluoride ions measured by the method of extrapolated differences using mercury as a standard are shown in Table II. Neither Ce₂F₆⁺ nor La₂F₆⁺ parent ions was observed. A small concentration of LaF₃⁺ may have been present that could not be observed because the background mercury peak has the same mass number as the expected peak for LaF₃⁺.
The heat capacities used in the calculations involving cerium fluoride were $C_p(s) = 17.90 + 10.14 \times 10^{-3} T + 1.10 \times 10^5 T^{-2}$ cal/deg/mole of CeF$_3$(s) as measured by King and Christensen and $C_p$ (monomer) = $20.214 + 0.477 \times 10^{-3} T - 2.629 \times 10^5 T^{-2}$ cal/deg/mole of CeF$_3(g)$ which was estimated by Lim and Searcy. If new heat capacity data of Charlu, et al. had been used in the various calculations, the enthalpy of vaporization of the monomer, for example, would be decreased by less than 0.03 kcal/mol in the experimental temperature range. The heat capacity of solid LaF$_3$ has recently been measured; use of this experimentally measured heat capacity changes the dimerization values from those that would be obtained by use of the heat capacities estimated by Mar and Searcy by less than 0.2% at 1577°K. Following Skinner and Searcy, the heat capacity of the dimer for both systems was estimated to exceed two times the heat capacity of the monomer by 4 cal/deg/mole.

All of the data points, with the points that were discarded darkened in, are shown in Fig. 1. The second law enthalpies and entropies of vaporization calculated without correction for $\Delta C_p$ from least squares fits of the data grouped by individual runs and combined are shown in Table III.

The enthalpy of sublimation of CeF$_3(g)$ was assumed to be 3.9 kcal less than the enthalpy of sublimation of LaF$_3(g)$ found by Mar and Searcy at 1495°K. Their value at 1477°K was used to normalize the LaF$_3(g)$ data. The pressure measured for CeF$_3(g)$ at 1495°K by Lim and Searcy was accepted. The thermodynamic functions at 1577°K corrected for heat capacity changes by means of Sigma calculations are summarized in Table IV. These values were calculated on the assumptions that Ce$_2$F$_5$
and La$_2$F$_5^+$ are the principal fragments produced by collision of 70 eV energy electrons with Ce$_2$F$_6$ and La$_2$F$_6$ and that the measured temperature dependences for Ce$_2$F$_5$ and La$_2$F$_5^+$ correctly reflect the partial pressures of Ce$_2$F$_6$ and La$_2$F$_6$. The second of these assumptions is rejected in the concluding section of this paper. The error limits quoted thus far have been the standard deviations from the least square fits and have included no estimate of the actual experimental errors.
The first and most obvious conclusion to be drawn from the present work is that the intensity ratios for ion peaks of CeF$_3$ and LaF$_3$ are essentially equal and show an essentially identical temperature dependence. (See Table IV.) Thus the additional electron on each cerium atom does not make Ce$_2$F$_6$(g) more stable than La$_2$F$_6$(g) relative to fragmentation and the problem of evaluation of pressures of Ce$_2$F$_6$(g) from intensity data is the same as for La$_2$F$_6$(g).

A completely unambiguous evaluation of dimer stabilities is not possible from present information for either system, but the evidence now weighs strongly against the interpretation given by Skinner and Searcy. They noted that their measured entropy of dimerization of La$_2$F$_6$ differed markedly from entropies of analogous reactions and pointed out that the fragmentation behavior of mixed metal halides supported the conclusion that the major ion fragment of the dimer could be LaF$_2$$^+$, which would be masked by the monomer peak. They accepted their measured heat of vaporization of La$_2$F$_6$ as correct, but obtained a corrected pressure by assuming that the entropy of dimerization should be the same as the entropy of dimerization measured for Al$_2$F$_6$(-35 eu/mol of dimer). This required increasing the experimentally measured entropy of vaporization of the La$_2$F$_6$ by about 11 eu/mol of La$_2$F$_6$. This increase was effected by multiplying all the apparent dimer pressures by a constant factor of about 250. To make the same normalization using the present LaF$_3$ data, the entropy of dimerization of La$_2$F$_6$ would have to be increased by about 7 eu which would require that the pressure of the La$_2$F$_6$ be multiplied by a factor of about 35. To increase the dimerization entropy of Ce$_2$F$_6$ to...
-35 would require a 6 eu increase in the entropy of vaporization of Ce₂F₆ which could be achieved by multiplying the Ce₂F₆ pressure by a factor of about 20.

Unobservable fragmentation of the kind suggested by Skinner and Searcy is a possible source of error that should be considered in evaluating any mass spectrometer polymer data. But Büchler, Feather, and Searcy¹⁶ have recently shown for conditions under which Al₂Cl₆(g) is known to be the major vapor species for aluminum chloride that Al₂Cl₅⁺ ion intensities exceed AlCl₂⁺ intensities by a factor of six. This result does not eliminate the possibility of extensive fragmentation for lanthanide element fluorides, but does make it seem less likely. The present dimerization entropies are closer to the expected values than is the value measured by Skinner and Searcy. Thus smaller errors in measured relative temperature dependences would bring the dimerization entropies to the expected values. The mere fact that there is a discrepancy between the two sets of data for La₂F₆ requires recognition that large errors in the heats of vaporization of the dimer are possible.

Furthermore, the present study shows clear evidence that high pressure intensity measurements deviate systematically downward from data extrapolated from lower pressure measurements, with the deviation of the dimer being greater than for the monomer. The same type of downward deviation at high pressures has also recently been seen by Feather and Searcy¹⁷ in a mass spectrometric study of low intensity sodium chloride polymers.
A systematic error that would cause the dimer intensity measurements to deviate downward more sharply with increased temperature than monomer intensities is unexpected in terms of presently recognized limitations of mass spectrometer measurements. The main expected sources of systematic error at high pressures are systematic temperature errors, saturation of the ion detectors, and deviation of the vapor from Knudsen flow toward hydrodynamic flow. A systematic temperature error should not show the selective effect on dimer data that was observed. Saturation of the ion detector should selectively introduce error in monomer measurements at high pressures rather than in dimer measurements. Onset of hydrodynamic flow has been demonstrated\textsuperscript{18,19} to produce deviations of measured pressures upward from extrapolations of low temperature data rather than downward. Under some experimental conditions, however, some indication of dips in the curve of experimental data below the extrapolated curves have been reported.

Studies by Carlson, Gilles, and Thorn\textsuperscript{19} of effusion from cells of different orifice geometries show that the total rate of effusion increases above that expected from the molecular flow equation when measurements are made at too high a pressure for a particular orifice. The magnitude of this effect depends on the length of the orifice. For the higher length L of orifice to radius R of orifice rations, a small dip of the measured pressures below the vapor pressures extrapolated from the Knudsen flow range was observed as the pressure in the cell increased. As the pressure was still further increased, the measured pressures increased above the extrapolated vapor pressures. This dip was not observed for a near ideal orifice (L/R = 0.07). As the authors
pointed out, since the magnitude of the dip is within their experimental error, the dip may not be real for any of the values of L/R they studied, although a similar dip has been reported by other authors\textsuperscript{20} in experiments on permanent gases for values of L/R much greater than used in the mass spectrometer studies.

Schulz and Searcy\textsuperscript{18} in an investigation of the total momentum of equilibrium vapor in torsion effusion for orifices of L/R values from 1 to 4 saw only a deviation upward of measured pressures from the extrapolated low pressure curves. Stickney, et al.\textsuperscript{21} have studied the angular distribution of cesium vapor beams from orifices of different lengths. The centerline intensities for a near ideal orifice (L/R = 0.08) were found to increase above the values expected for Knudsen flow as the pressure was raised. For longer orifices of the same radius, the centerline intensities first dropped below the values expected for molecular flow, then as the pressure was further increased, the intensities increased above those expected for Knudsen flow. Other authors\textsuperscript{22-25} have reported similar findings.

Velocity distributions in the transition region have also been measured,\textsuperscript{25-28} and it has been reported that when Knudsen flow conditions are violated for non-ideal orifices, the velocity distribution is distorted from Maxwellian with too few low speed or too many high speed molecules effusing in the forward direction. Since the total masses that effused were not measured, these two possibilities could not be distinguished. The distortion becomes greater as the L/R ratio of the orifice is increased.
Thus there may be a transition range in which a slight dip below the extrapolated pressures can occur, especially in the direction normal to the orifice. But an effect at the orifice that would alone be enough to explain the data of Fig. 1 seems unlikely.

Scattering of the vapor molecules after they leave the cell, however, could cause the observed behavior. Troitskii has concluded on the basis a theoretical analysis that the mean free path for molecules in a beam is only three times that for the molecules in an equilibrium vapor of the same density. Brewer, Berg, and Rosenblatt observed collision quenching in iodine vapor beams that were qualitatively consistent with expectations from Troitskii's calculations.

David Meschi has recently calculated the collision probability for monomers and dimers in a beam formed by effusion of an ideal gas at equilibrium through an orifice. Because in our study the dimer concentration in the beam is much lower than the monomer concentration, a given number of monomer-dimer collisions will scatter a larger fraction of the dimers in the beam than of the monomers. The results, which should be reliable to within an order of magnitude predict that dimer scattering should exceed monomer scattering and should become observable at about the apparent pressures that we observe.

The more limited dimer data of Skinner and Searcy do not show the clear evidence of curvature in the \((I^+/T)\) plots for the dimer that is found in the present study. But the difference in temperature dependence in the fraction of dimer molecules scattered could easily result from the differences in orifice geometries and collimating geometries between the studies.
That some factor such as selective scattering from the beam influenced the Ce₂F₆(g) intensity measurements at the higher pressures is clearly shown by Fig. 1. Table V summarizes second law heats calculated for Ce₂F₆ from our best two runs when dimer intensity measurements beginning at the highest temperature of accepted monomer data are successively eliminated. The calculated heats of sublimation of dimer rise systematically as the high pressure data are eliminated.

The calculations of Table V when coupled with Meschi's calculation that selective scattering of dimers should become important in the pressure range of our study, convince us that the measured dimer temperature dependence for Ce₂F₆ is lower than the true temperature dependence of dimer partial pressure. Too few data for the sublimation of La₂F₆ were collected in either study for a similar analysis to be made, but the close similarity between the two systems supports the same conclusion for the La₂F₆ dimer.

In light of the demonstration ¹⁶ that the principal ion fragment for Al₂Cl₆ does not coincide with the monomer peak, we accept the conventional assumptions for converting ion intensities to pressures and we accept as the probable value for the entropy of dimerization in each system -35 ± 4 eu for our experimental range. This leads to -51.5 ± 7 kcal for enthalpy of dimerization of CeF₃(g) and to -54.2 ± 7 kcal for dimerization of LaF₃ at 1577°K.
REFERENCES

### Table I. Orifice Dimensions

<table>
<thead>
<tr>
<th>Orifice</th>
<th>Geometry</th>
<th>Dimensions, mm</th>
<th>Thickness, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>circular</td>
<td>1.00, dia</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>circular</td>
<td>0.25, dia</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>rectangular</td>
<td>3.16 x 0.99</td>
<td>1.15</td>
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</table>
### Table II. Appearance potentials and fragmentation patterns.

<table>
<thead>
<tr>
<th>Ion (M = Ce or La)</th>
<th>Appearance Potentials for CeF₃ Ions (eV)</th>
<th>CeF₃ Ion Intensities at 1473°K Relative to CeF₂⁺ = 1000</th>
<th>LaF₃ Ion Intensities at 1600°K Relative to LaF₂⁺ = 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁺</td>
<td>25.2</td>
<td>128.</td>
<td>108.</td>
</tr>
<tr>
<td>MF⁺</td>
<td>17.2</td>
<td>190.</td>
<td>199.</td>
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<td>MF₂⁺</td>
<td>13.5</td>
<td>1000.</td>
<td>1000.</td>
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<tr>
<td>MF₃⁺</td>
<td>11.4</td>
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<td>0.</td>
</tr>
<tr>
<td>M₂F₅⁺</td>
<td>13.1</td>
<td>0.05</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*See text.*
Table IIIA. Enthalpies and Entropies of vaporization of cerium fluoride calculated without making heat capacity corrections.

<table>
<thead>
<tr>
<th>Orifice #</th>
<th>No. of Data Points</th>
<th>Temp. Range (°K)</th>
<th>$\Delta H_v$ (kcal/mole CeF$_3$)</th>
<th>$\Delta S_v$ (eu/mole CeF$_3$)</th>
<th>No. of Data Points</th>
<th>Temp. Range (°K)</th>
<th>$\Delta H_v$ (kcal/mole Ce$_2$F$_6$)</th>
<th>$\Delta S_v$ (eu/mole Ce$_2$F$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomer (CeF$_3$)</strong></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>16</td>
<td>1524-1274</td>
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<td>7</td>
<td>1522-1437</td>
<td>132.6±4.6</td>
<td>47.7±3.2</td>
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<tr>
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<td>1513-1283</td>
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<td>6</td>
<td>1509-1429</td>
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<td>12</td>
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<td>5</td>
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<td>1586-1391</td>
<td>95.3±0.4</td>
<td>43.4±0.3</td>
<td>5</td>
<td>1581-1590</td>
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<td>35.8±2.4</td>
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<tr>
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<td>15</td>
<td>1523-1262</td>
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<td>45.4±0.3</td>
<td>11</td>
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<td>50.6±1.2</td>
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<tr>
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<td>45.3±0.3</td>
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<tr>
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<td>9</td>
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<td>44.4±2.6</td>
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<tr>
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<td>19</td>
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<td>43.4±0.4</td>
<td>12</td>
<td>1676-1498</td>
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<td>13</td>
<td>1577-1393</td>
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<td>47.2±1.4</td>
</tr>
<tr>
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<td>44.6±0.4</td>
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<td>1572-1397</td>
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<td>67</td>
<td>1676-1393</td>
<td>125.4±0.9</td>
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</table>
Table IIIB. Enthalpies and entropies of vaporization of lanthanum fluoride calculated without making heat capacity corrections.

<table>
<thead>
<tr>
<th>Orifice #</th>
<th>No. of Data Points</th>
<th>Temp. Range (°K)</th>
<th>$\Delta H_v$ (kcal/mole LaF$_3$)</th>
<th>$\Delta S_v$ (eu/mole LaF$_3$)</th>
<th>No. of Data Points</th>
<th>Temp. Range (°K)</th>
<th>$\Delta H_v$ (kcal/mole La$_2$F$_6$)</th>
<th>$\Delta S_v$ (eu/mole La$_2$F$_6$)</th>
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</thead>
<tbody>
<tr>
<td>Selected Data</td>
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<td></td>
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<tr>
<td>1</td>
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<td>1564-1326</td>
<td>98.1±0.7</td>
<td>43.1±0.5</td>
<td>9</td>
<td>1562-1443</td>
<td>128.8±1.3</td>
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</tr>
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<td>12</td>
<td>1644-1400</td>
<td>95.0±0.4</td>
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<td>1645-1523</td>
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<td>42.5±1.5</td>
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<tr>
<td>Combined</td>
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<td>1644-1326</td>
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<td>42.5±0.3</td>
<td>16</td>
<td>1645-1443</td>
<td>129.6±0.9</td>
<td>43.2±0.6</td>
</tr>
<tr>
<td>All Data</td>
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<td>1654-1326</td>
<td>96.0±0.9</td>
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<td>94.7±0.3</td>
<td>40.8±0.2</td>
<td>10</td>
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<td>42.2±0.8</td>
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<tr>
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<td>1706-1326</td>
<td>96.1±0.5</td>
<td>41.7±0.4</td>
<td>22</td>
<td>1707-1443</td>
<td>127.8±1.1</td>
<td>42.1±0.7</td>
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<td>Thermodynamic Quantity</td>
<td>LaF$_3$ Data</td>
<td>CeF$_3$ Data</td>
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<td></td>
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<td></td>
<td></td>
</tr>
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<tr>
<td></td>
<td>Mar and Searcy$^6$</td>
<td>Skinner and Searcy$^1$</td>
<td>Present Study</td>
<td>Lim and Searcy$^5$</td>
<td>Present Study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H_v$ Monomer (kcal)</td>
<td>98.4</td>
<td>96.7</td>
<td>96.1</td>
<td>92.7</td>
<td>95.8</td>
<td></td>
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<tr>
<td>$\Delta H_v$ Dimer (kcal)*</td>
<td>-</td>
<td>122.1</td>
<td>128.8</td>
<td>-</td>
<td>131.5</td>
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<td></td>
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<tr>
<td>$\Delta H$ Dimerization (kcal)*</td>
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<td>-71.3</td>
<td>-63.4</td>
<td>-</td>
<td>-60.1</td>
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<tr>
<td>$\Delta S_v$ Monomer (eu)</td>
<td>43.1</td>
<td>42.0</td>
<td>41.8</td>
<td>41.5</td>
<td>43.7</td>
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</tr>
<tr>
<td>$\Delta S_v$ Dimer (eu)*</td>
<td>-</td>
<td>38.4</td>
<td>42.8</td>
<td>-</td>
<td>46.8</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\Delta S$ Dimerization (eu)*</td>
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<td>-45.6</td>
<td>-40.8</td>
<td>-</td>
<td>-40.6</td>
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</tbody>
</table>

* Calculated on the assumption that dimer intensities are valid measures of pressure over the same temperature range as monomer intensities, but see Discussion Section.
Table V. Heats of vaporization for two runs calculated by successively removing the data points taken at the highest pressures.

<table>
<thead>
<tr>
<th># points removed</th>
<th>CeF₃(g)</th>
<th>Ce₂F₆(g)</th>
<th>CeF₃(g)</th>
<th>Ce₂F₆(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96.1±0.5</td>
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<td>96.0±0.4</td>
<td>132.2±1.9</td>
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<tr>
<td>1</td>
<td>95.8±0.4</td>
<td>135.0±2.0</td>
<td>96.0±0.4</td>
<td>134.5±1.6</td>
</tr>
<tr>
<td>2</td>
<td>95.9±0.5</td>
<td>136.3±2.2</td>
<td>96.0±0.5</td>
<td>135.6±1.9</td>
</tr>
<tr>
<td>3</td>
<td>95.7±0.5</td>
<td>135.8±2.7</td>
<td>96.1±0.5</td>
<td>137.4±2.1</td>
</tr>
<tr>
<td>4</td>
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<td>96.1±0.6</td>
<td>139.3±2.7</td>
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<tr>
<td>5</td>
<td>95.6±0.7</td>
<td>138.9±4.8</td>
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<td>142.1±4.1</td>
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<tr>
<td>6*</td>
<td>95.2±0.7</td>
<td>133.3±5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Points were removed until only 5 dimer data points remained.
Fig. 1. Vaporization data for cerium trifluoride. Open symbols indicate selected data (see text).
Figure 1

![Graph showing vapor pressure as a function of 1/T (x10^4) (°K⁻¹)]
PART 2

THE VARIATION WITH TEMPERATURE OF THE CONGRUENT VAPORIZATION COMPOSITION OF GALLIUM SESQUISULFIDE

\( \text{Ga}_2\text{S}_3 \)
I. INTRODUCTION

Thermodynamic data gathered by dynamic vapor pressure techniques usually must be collected under conditions where the pressures measured are not functions of time but only of temperature. For two component systems, a group of materials that satisfies this requirement is two phase mixtures and single phases that vaporize to a gas of the same overall composition as the solid (vaporize congruently). Many studies of congruently vaporizing solids have been conducted. However, the fact that the composition for congruent vaporization may change with temperature is generally ignored. In most instances the composition changes are small and their neglect probably has no influence, to within experimental accuracy, on the quantities being determined, such as the heat of vaporization and total vapor pressure.

However reasonable this supposition may be, it seems desirable to obtain experimental data on the variation with temperature of the composition of congruent vaporization for at least a few solids of relatively narrow composition limits and, if possible, to experimentally examine the effect of the composition variation on the partial pressure of each vapor species. Apparently no such information has yet been obtained.

The mass spectrometer is an obvious choice for such a study since each vapor species can be individually monitored. The mass spectrometric method has been used previously to obtain pressure vs composition data by Sidorov et al. and by Miller and Searcy. Both studies concentrated on observing the gross changes of the composition of samples of various starting compositions as the composition changed over considerable ranges to the congruent composition. Some attempt was made by
Miller and Searcy to observe the change in congruent composition brought about by a change in temperature but the results were scanty and inconsistent.

The ideal substance for such an investigation should satisfy at least three criteria: (1) In order to avoid the uncertainties in absolute pressure determination associated with the mass spectrometric technique, the total vapor pressure should be known; (2) The substance should vaporize congruently but should exhibit some measurable shift in the actual congruent composition with temperature; (3) The compound should dissociate on vaporization to a simple gas composition, preferably to only two different major vapor species.

Whether a measurable shift in congruent composition will take place with changing temperature for any particular solid could not readily be predicted since only the fragmentary study on indium sesquisulfide (In$_2$S$_3$) by Miller and Searcy$^2$ was available as a guide. That solid did not promise to be a satisfactory substance for study because the available data suggested that two different phase transitions may occur in the temperature range suitable for mass spectrometer study.

Cadmium sulfide (CdS) was tested as a possible substance for study but composition changes proved too small to measure. Gallium sesquisulfide (Ga$_2$S$_3$) was tried next and proved suitable for the study. It is the gallium sesquisulfide results which are the subject of this paper.

Previous work on the gallium sesquisulfide phase indicates that it exists in three crystalline modifications: an ordered high temperature structure, $\alpha$; a disordered high temperature structure, $\beta$; and a low temperature modification, $\gamma$.$^3$ The transition temperatures are badly
defined. The $\gamma$ to $\alpha$ transition is reported to be between $820^\circ K$ and $870^\circ K$. This transformation is of no importance here since all measurements were made at much higher temperatures.

The $\alpha$ to $\beta$ disordering transformation temperature is reported by Rustamov et al.\textsuperscript{5} to be a $1285\pm 10^\circ K$ from differential thermal analysis work. Lieth et al.\textsuperscript{6} reported no thermal arrest for stoichiometric solid gallium sesquisulfide but do report a thermal effect for the less than 60 a/o S material which they think is due to a phase change at $1100^\circ K$.

The melting point of gallium sesquisulfide was reported to be about $1520^\circ K$ in an early study by Klemm and von Vogel.\textsuperscript{7} This is disputed in the more recent studies of Lieth et al.\textsuperscript{6} and Rustamov et al.\textsuperscript{5} who report that stoichiometric gallium sesquisulfide melts congruently at $1360^\circ K$ and $1390^\circ K$ respectively. The stability range of solid gallium sesquisulfide was reported to extend from 59 to 60 a/o S with no range of solubility on the sulfur rich side of the stoichiometric composition.\textsuperscript{5}

Spandau and Klanberg,\textsuperscript{8} using a transportation technique, report that above $1220^\circ K$ gallium sesquisulfide loses sulfur and continues to lose sulfur as the temperature is increased further. Samples cooled from as high as $1570^\circ K$ had 55 a/o S and showed a diffraction pattern which was attributed to a $\text{Ga}_4\text{S}_5$ phase that was assumed to have a variable composition. It is not stated whether or not these samples had melted, but the current work and all other pertinent past studies indicate that they must have melted. There is disagreement as to the existence of the $\text{Ga}_4\text{S}_5$ phase.
II. EXPERIMENTAL

The experiments were carried out in a magnetically focused 60° sector 24 cm radius Atlas mass spectrometer. Ions were created by electron impact (70 eV) and detected with a 16 stage copper-beryllium electron multiplier. Samples were contained in either alumina or graphite effusion cells which were held in an outer molybdenum cell. The orifice dimensions are given in Table I.

The cells were heated by radiation and electron bombardment from a tungsten wire filament. Temperatures were measured with a platinum-platinum 10% rhodium thermocouple clamped into a hole in the bottom of the molybdenum cell. The cell was lowered below the center of the hot zone to a position at which condensation on upper parts of the cell and the lid was eliminated.

The temperature scale was calibrated by making a second law determination of the heat of vaporization of silver and by observing the apparent melting point of silver. When the cell which contained the solid silver was heated to a temperature just above the melting point of silver, the temperature of the silver itself could not follow that of the cell until the silver had melted. If the temperature of the cell were raised just slightly above the melting point, the measured ion intensity of silver would reach a constant value then, with no measurable increase in temperature of the cell, the ion intensity of silver would rapidly increase to a new constant value when melting was completed and the silver could equilibrate with the rest of the system.

The time at temperature before observing this increase and the magnitude of the increase are indicative of the extent to which the cell
temperature was above the transition temperature. By holding the cell at a temperature where this increase is small, it is possible to get an *in situ* check of the absolute accuracy of the temperature measuring system to within ± 3°K at the melting point of silver (1234°K). This one calibration point plus a second law heat determination give a better check of the temperature measurement accuracy and offer a better opportunity for correction than is possible with just a second law measurement.

With the cell in the center of the hot zone, the measured temperature agreed to within 2°K of the literature value for the melting point of silver. After the cell was positioned to eliminate condensation on the lid, the apparent melting point of silver was found, when measured from time to time during the course of the experiments, to be 1222, 1221, 1225, 1222, and 1222°K. The average, 1222°K, is 12°K below the literature value. The apparent melting point is believed to be low because the bottom of the molybdenum cell into which the thermocouple was inserted was colder than the higher portion of the molybdenum cell which held the liner that contained the silver.

The second law heat of vaporization of silver was measured over approximately the same temperature range that was used in the gallium sesquisulfide experiments. The few points measured above the melting point of silver were corrected to allow for the literature value of the heat of fusion (2.7 kcal/mole) before heats of sublimation were calculated from the slope of the log IT vs 1/T line.

Heats of vaporization calculated for silver using the temperatures as measured are 65.2 ± 0.2 and 64.2 ± 0.5 kcal/mole for temperature
ranges of 1106-1343 and 1159-1339°K respectively. Adding a constant 12°K to all the measured temperatures and recalculating the heats gives values of 66.6 ± 0.2 and 65.6 ± 0.5 kcal/mole for temperature ranges of 1118-1355 and 1171-1351°K respectively. The literature value is 66.2 kcal/mole at 1234°K. In light of this good agreement which resulted from the constant 12°K correction, all temperatures presented below and used in any calculations involving gallium sesquisulfide have been corrected by 12°K.

High purity gallium sesquisulfide proved difficult to obtain. Samples supplied by Atomergic Chemetals Co. and K+K Laboratories, Inc., when heated in the mass spectrometer, showed Ga₂O⁺ ion intensities fully 1/3 of the Ga₂S⁺ intensities. (Ga₂S⁺ and S₂⁺ are the principal ions present in the mass spectrum over pure Ga₂S₃.) The Ga₂O⁺ did not arise from reaction with the alumina liner since it was also seen when a graphite liner was used.

We tried to synthesize gallium sesquisulfide by heating the correct stoichiometric quantities of gallium and sulfur in an evacuated quartz tube. Samples heated for up to one week at 720°K, approximately the normal boiling point of sulfur, showed very little, if any, reaction product. This lack of reaction has been referred to by some other authors who successfully completed the synthesis by keeping the ends of their quartz reaction tubes at different temperatures.

We succeeded in synthesizing high purity gallium sesquisulfide by using the replacement reaction 3CdS(s) + 2Ga(l) = Ga₂S₃(s) + 3Cd(g). This reaction proceeded well in vacuum at 1000°K and also in a sealed quartz tube where one end was kept cool to condense the cadmium vapor.
After the reaction was completed at 1000°K, the more refractory product gallium sesquisulfide was heated to a higher temperature to vaporize any excess cadmium sulfide. This process could be easily followed when the reaction was carried out in the mass spectrometer.

Although this synthesis was successful, care was required not to introduce any oxygen. For example, the reaction when carried out with purified grade cadmium sulfide from one supplier, yielded a large $\text{Ga}_2\text{O}^+$ ion peak. High purity 99.999% cadmium sulfide, supplied by Research Organic/Inorganic Chemical Corp., yielded gallium sesquisulfide samples that showed very little $\text{Ga}_2\text{O}^+$.

After this synthesis had been worked out, we obtained from Alpha Inorganics gallium sesquisulfide which was as good or better ($\text{Ga}_2\text{O}^+$/Ga$_2$S$^+$ ion intensity ratio less than 0.01 and proper X-ray pattern) than the material we could produce. All work reported here was done with the Alpha Inorganics gallium sesquisulfide. A semi-quantitative spectroscopic analysis revealed only these impurities:

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
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<td>0.002</td>
</tr>
<tr>
<td>Si</td>
<td>0.015</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0005</td>
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<tr>
<td>Ag</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.0005</td>
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</tbody>
</table>

To obtain reproducible starting compositions for our experiments, all as received material was heated to constant $\text{S}_2^+$/Ga$_2$S$^+$ flux ratios at ∼1270°K in an alumina cell in the mass spectrometer. This initial heating showed the as received material to be sulfur rich as compared to the congruently vaporizing composition at the temperatures of our experiments.
A 0.6 gm sample which had been equilibrated at 1270°K and rapidly cooled was analyzed for sulfur by the Grote combustion method. Two analyses gave 40.53 and 40.56 w/o S. If the original sample is assumed to have contained only sulfur and gallium, this converts to an average of 59.72 a/o S. If the residue after combustion was assumed to be pure Ga₂O₃, the weight percent of gallium plus sulfur was calculated to be 100.88 and 101.00 w/o for the two determinations. The cause of this discrepancy is unknown but since only the analysis for sulfur was specific and the spectroscopic analysis of the original materials showed no substantial impurities, we assume the congruently vaporizing composition at 1270°K to be 59.72 a/o S and 40.28 a/o Ga.

For converting intensity versus time measurements to pressure versus composition data, accurate measurements of sample weight changes were needed. Accordingly, considerable effort was expended to eliminate extraneous sources of weight change. The empty cells and lids were baked out in the mass spectrometer at temperatures above the maximum temperature to be used in a run to assure removal of any material remaining from a previous run. After baking, the cells were allowed to cool in vacuum, then the vacuum chamber was vented with dry nitrogen and the liner was removed from the molybdenum holder and weighed. The sample, which had previously been equilibrated at 1270°K, was introduced and the liner and sample were weighed.

The liner and lid were replaced in the molybdenum cell holder and the molybdenum lid was replaced. The molybdenum cell was never removed from its tungsten support rods so the thermocouple did not have to be disturbed. This precaution assured that the temperature calibration, as
evidenced by the silver results, remained constant from run to run. The single layer tantalum heat shield that surrounded the heating assembly was replaced and the flange holding the cell was reinstalled in the mass spectrometer. The mass spectrometer, after being slowly evacuated to assure that no sample would blow out of the cell, was baked overnight.

After a run, the liner and remaining sample were weighed. Between the initial bake out of the empty cell and the final weighing after the run, the cell was handled only with tweezers. All weighing was done on a Mettler H20T balance. Weights were recorded to an accuracy of $1 \times 10^{-5}$ gm, and weight losses are probably accurate to at least $\pm 1 \times 10^{-4}$ gm. A check of the effect of the entire procedure on measured weight changes was made by weighing an empty alumina liner, heating it four hours at $1300^\circ$K, and weighing. Weights of 1.99912 gm before and 1.99912 gm after heating in the mass spectrometer were obtained.

To demonstrate that some species such as adsorbed water, which could evaporate at relatively low temperatures, did not contribute significantly to the weight loss, a sample of about 0.4 gm, which is about four times the weight used in most runs, was placed in an alumina cell. The entire experimental procedure, excluding any high temperature heating, but including a low temperature anneal of two hours at $950^\circ$K was followed. The measured weight of the liner and the sample was 2.43256 gm before and 2.43257 gm after the run. Since the minimum weight loss recorded in any of the quantitative runs was greater than 0.01 gm and usually much greater, the weighing procedure and sample handling procedure were not significant sources of error.
The anneal at 950°K was used in all experiments to drive volatile material from the hot zone. At 950°K the dissociation pressure of gallium sesquisulfide is too low (2 x 10^{-9} \text{ atm})^{13} to cause any weight change in the course of a few hours which could measurably effect the results. After the 950°K anneal, the cell could be heated rapidly to the experimental range, \( \approx 1270°K \), without causing a serious rise in background pressure.
III. RESULTS AND DISCUSSION

The ion species observed in this study and in a study by Uy et al. are listed in Table II. Uy et al. showed that Ga$_2^+$, Ga$^+$, GaS$^+$, and S$^+$ are mainly fragments from Ga$_2$S and S$_2$. That Ga$_2$S$^+$ and S$_2^+$ are not predominantly fragments is further confirmed by the observation of this study that the product of Ga$_2$S$^+$.S$_2^+$ remains nearly constant when the Ga$_2$S$^+$/S$_2^+$ ratio varies by as much as a factor of fifty.

In mass scans up to mass 1000 at the highest temperature studied, 1370°K, ion peaks not reported by Uy et al. were observed. At this high temperature the Ga$_2$S$_2^+$ intensity rose to 1.6% of the Ga$_2$S$^+$ intensity. The analogous ion, In$_2$S$_2^+$, was observed under comparable conditions by Miller and Searcy in their study of the indium sesquisulfide system.

Clusters of other ion peaks which were at least fifty times less intense than the Ga$_2$S$_2^+$ peak were also seen at 1370°K. These peaks appear to have the correct isotopic ratios for Ga$_3$S$^+$, Ga$_3$S$_2^+$, Ga$_3$S$_3^+$, and Ga$_4$S$_4^+$. Because the background for use in calibrating the mass spectrometer at these high mass numbers is low, definite mass identification was not made. No other shutterable species were observed. Small concentrations of non-shutterable S$_x^+$ (x<8) polymers, which probably arise from sulfur condensed near the ion source, were observed.

In a mass spectrometer using a Knudsen cell source $P_i = U_i I_i^+ T$ where $P_i$ is the vapor pressure of species $i$ within the cell, $U_i$ is an unknown constant dependent on the machine itself and on the particular species observed, $I_i^+$ is the ion intensity of species $i$, and $T$ is the absolute temperature. The stoichiometric vaporization reaction considered here is Ga$_2$S$_3$(s) = Ga$_2$S(g) + S$_2$(g) for which the equilibrium constant $K_p$ is
This expression can be rewritten in terms of the ion intensities as

$$K_p = (P_{Ga_2S})(P_{S_2}).$$

and from the slope of log \(I_{Ga_2S}^+ \cdot I_{S_2}^+ \cdot T^2\) vs 1/T the heat of reaction can be calculated by the second law method.

Table III gives the Ga$_2$S$^+$ and S$_2^+$ ion intensity vs temperature data of the two runs used to calculate second law heats. The data taken with orifice 3 represent the steady state values obtained in run 7 of the composition vs temperature runs (see below). Since the data taken with orifice 1 were not continuously recorded as a function of time, they could not be used for composition calculations. This, of course, did not remove the necessity of waiting until the composition stabilized before recording each data point.

Table IV gives the heats calculated from the individual slopes of the log \(I_{Ga_2S}^+ \cdot T\) and log \(I_{S_2}^+ \cdot T\) vs 1/T data for each run, from the log \(I_{Ga_2S}^+ \cdot I_{S_2}^+ \cdot T^2\) vs 1/T data for each run, and from the combined data. To calculate the combined value, the least squares fits of the log \(I_{Ga_2S}^+ \cdot I_{S_2}^+ \cdot T^2\) vs 1/T data for both runs were made to coincide at 1168°K, the overall mid point of the temperature range, by multiplying the \(I_{Ga_2S}^+ \cdot I_{S_2}^+ \) data of each run by the constant values noted in Table III. A least squares slope for all the data points was then calculated. This procedure gives 157.3 ± 0.5 kcal/mole of Ga$_2$S$_3$ for the heat of vaporization at 1168°K, the mid point of the temperature range, compared to the values of 161.7 determined by Kashkooli and Munir at 1237°K in a
torsion effusion study and the value of 153.2 determined by Uy et al. at 972°K in a mass spectrometric study.

These heats were all calculated assuming that the stoichiometric reaction was operative, and that the congruent composition did not change with temperature. As will be shown below, this is not strictly true. The data from this study show what is believed to be a phase change at 1230°K which is accompanied by a small shift of about 0.3 a/oS in the composition for congruent vaporization. If this change caused a significant change in the heat of vaporization, the plot of log

\[ \frac{I_{Ga_2S}^+ \cdot I_{S_2}^+ \cdot m^2}{2} \text{ vs } 1/T \]

would show a deviation from linearity. No noticeable deviations are observed in the data from this and the previous relevant study. Uy et al. would not have observed this phase change in their mass spectrometric study since all their measurements were made below 1020°K. It is concluded that the error introduced by ignoring the small composition change when calculating the heat of vaporization is within the experimental error of the available data and may be ignored.

The composition changes, especially the one accompanying the phase change, do make it tedious to take data for a second law calculation with a mass spectrometer. One must wait not only until the temperature stabilizes but also until the composition stabilizes before taking a point. Since the total pressure is not drastically affected while these changes occur and the effect decays slowly as the congruent composition is approached, this phase change may be nearly unobservable with effusion techniques where one cannot observe the ratios of the effusing species.
In the experiments to determine the congruent vaporization composition as a function of temperature, the intensities of Ga$_2$S$_5^+$ and S$_2^+$ ions were followed for each run as a function of time and temperature. As an example, the data from one run are plotted in Fig. 1. The temperature was held as constant as possible until steady state vaporizing conditions were observed. The power to the heating filament was then abruptly changed and measurements were taken until steady state was again reached. This process could be repeated as often as desired during a run. Since only one species could be observed at a time, measurements were made alternately with one peak always being monitored. The time between successive measurements of the same peak ranged from about 30 seconds, the minimum time required to make a measurement, to a maximum of 15 minutes. The shorter intervals were used during rapid changes, such as those immediately following a temperature change, and the longer intervals were used as the changes became less rapid and nearly linear for the time intervals utilized.

The same heating cycle was followed at the start of each run. As mentioned above, every sample at the start of a run was heated to about 950°K and held for at least one hour. The sample was then heated rapidly to a constant temperature at 1270 ± 7°K, and annealed at this temperature until a steady state vaporization situation was reached in order to assure that the starting composition for each run would be the same. During this time the final alignment of the cell and adjustment of the ion source optics were made. The initial annealing temperatures were not exactly the same in each run. This does not introduce any serious errors since they were all within ± 7°K of each other and, as is shown
below, the composition for congruent sublimation is not a strong function of temperature over this particular short temperature range.

The remainder of the temperatures visited during any run were not necessarily the same from run to run but were selected to examine various temperature ranges. On many runs the final data were taken at about the same temperature as the initial anneal to see if the measurements and subsequent calculations were self consistent and if the starting composition would be regained in the calculations.

The ratio $I_{S_2}^+ / I_{Ga_2S}^+$ was, in most cases, a good check on whether steady state congruent conditions had been reestablished after a temperature change because composition changes were usually less than 0.4 a/o and random variations in the steady state $I_{S_2}^+ / I_{Ga_2S}^+$ ratios with time were of the order of 5%. A small temperature change near the highest temperatures investigated, however, produced about a 3 a/o composition change so that steady state intensity ratios measurably depended on temperatures in that range.

One of the main difficulties in mass spectrometry is the problem of converting the observed ion intensities to absolute pressures. This conversion is not needed for the calculation of second law heats described above, but it is needed for the calculation of the total number of moles of each species effused from a cell which in turn is needed for the calculation of composition changes of the solid. The difficulties can be separated into two main categories: Those associated with the mass spectrometer itself, and those arising from the nature of the mass spectrometric method.
The first category concerns the overall machine geometry and sensitivity which may generally be assumed constant during any particular run for all species, but which may change from run to run. For a congruently vaporizing solid of known composition and total pressure, if the ions which arise solely from each principal vaporizing species can be identified, the constants for converting intensities to pressures for each ion can be readily calculated by assuming the composition and total pressure to be known at a single temperature. These constants can then be used to determine absolute pressures from ion intensities when the experimental conditions are changed so that congruent vaporization no longer occurs. The procedure is outlined below.

The total pressure over congruently vaporizing gallium sesquisulfide is known from the torsion effusion study of Kashkooli and Munir, and the composition has been determined for 1270°K by chemical analysis. If the solid composition is written as Ga$_{1-x}$S$_x$ (x = 0.5972 at 1270°K) the congruent vaporization reaction is

$$Ga_{1-x}S_x(s) = (1-x)/2 \ Ga_2S(g) + (3x-1)/4 \ S_2(g)$$

(1)

or

$$\frac{J_{S_2}}{J_{Ga_2S}} = \left( \frac{3x-1}{4} \right) \left( \frac{1-x}{2} \right)$$

(2)

where $J_{S_2}$ and $J_{Ga_2S}$ are the molecular fluxes of $S_2$ and $Ga_2S$ respectively.
From the Langmuir equation

\[ J_i = \frac{P_i}{\sqrt{2\pi M_i RT}} \cdot A \cdot w \]  

(3a)

where \( J_i \) = flux of species i
\( P_i \) = partial vapor pressure of species i
\( M_i \) = molecular wt. of species i
\( R \) = gas constant
\( T \) = temperature
\( A \) = orifice area
\( w \) = Clausing factor.

Substituting values for the constants

\[ J_i = \frac{P_i}{\sqrt{M_i}} \cdot A \cdot 44.33 \]  

(3b)

where the units are:

\( J_i \) = moles/sec
\( P_i \) = atm
\( M_i \) = gm/mole of molecule i
\( T \) = °K
\( A \) = cm²

Equations (2) and (3) can be combined with the expression for the total pressure \( P_T = P_{S_2} + P_{Ga_2S} \) so that the partial pressure of each component can be written in terms of the total pressure.
The proportionality constant $U_i$ for converting the intensities to absolute pressures in the equation $P_t = U_1 I_1^T$ can then be written as:

$$U_{S_2} = \frac{P_t}{I_{S_2}^T \left(1+\frac{1}{F}\right)}$$

(5)

$$U_{Ga_2S} = \frac{P_t}{I_{Ga_2S}^T \left(1+\frac{1}{F}\right)}$$

where all the values are at temperature $T$ and $I_1^f$ is the ion intensity actually measured during congruent vaporization. The values of $U_{S_2}$ and $U_{Ga_2S}$ determined in this way may then be used when conditions are changed from those for congruent vaporization. The constants, however, must be redetermined in each run to correct for machine variables such as electron multiplier gain that may change from run to run. These constants can be redetermined during the run whenever the sample is vaporizing congruently, as long as the composition and total pressure are known. Once the constants have been determined, the effusion rate of a species
is then readily calculated by means of the Langmuir equation written in terms of the ion intensities:

$$J_1 = \frac{I^*_\text{TU}}{\sqrt{MT}}$$

The moles of i effused in a time interval is merely the effusion rate multiplied by the time. In the present study, the measured intensities were first converted to effusion rates for the two effusing species (S₂ and Ga₂S). The number of moles of each molecule effused during any time interval was then calculated by integrating the effusion rate vs time curve assuming linear variations between the experimental points. The number of moles of sulfur and gallium calculated to have effused was subtracted from the initial moles of each in the solid and the solid composition recalculated. To determine the composition of congruent vaporization as a function of temperature, calculations of the composition were made at times when the sample had reached steady state.

The composition of the solid at room temperature and just after reaching the reference temperature, 1270°K, are somewhat in doubt even though all samples had been previously annealed to steady state at this temperature because some change in composition could occur during heating or cooling. To eliminate this uncertainty, the reference composition for each run is taken as the composition after steady state had been reached and maintained for some time (\(\sqrt{1/2}\) to 1 hour) at 1270°K and just before the temperature was changed to its next value. The composition at that time was assumed to be the 59.72 a/oS from the chemical analysis.
Run 7, which will be discussed separately, is a unique exception to this procedure since it was carried out entirely at lower temperatures. The moles of material effused before this time calculated from the intensity, temperature, time data, which were recorded as soon as the intensities of shutterable ion peaks were measurable, were merely subtracted as to their calculated weight from the weight of the sample before the experiment was started to give a corrected initial weight. This corrected initial weight of the sample was then assumed to have a composition of 59.72 a/o S.

As mentioned above, the $U_i$ correction factors can be calculated from Eq. (5) as long as the total pressure and the composition of the solid are known and the sample is vaporizing congruently. The $U_i$ determined for steady state at 1270°K can be used for the entire run.

Another method is to redetermine $U_i$ every time the sample had returned to congruently vaporizing conditions. The problem here is that the composition for congruent vaporization is not known at other temperatures. But the total pressure, as shown in the equilibrium runs in this and the previous study, is not noticeably changed from normal straight line behavior in a log P vs 1/T plot by the small composition variations seen here. Thus, if the composition can be calculated, the $U_i$ can be determined, and on the other hand, if the $U_i$ can be calculated, the composition can be calculated. To get around this problem, an iterative method was used in which the mole fraction of sulfur, "x" in Eq. (5), was assumed equal to 0.5972 in order to calculate provisional values of $U_i$. The composition of the solid was then calculated with the provisional values of $U_i$. The value of x was then replaced by this new
calculated solid composition and the calculation repeated. This procedure was repeated until the value of x used to calculate $U_i$ and the solid composition calculated using these values of $U_i$ agreed to within 0.0001.

The samples were weighed before and after a run to determine a measured weight loss. This measured weight loss was compared to the calculated weight loss from the effusion data (see Table V). In all cases, the measured weight loss was greater than the calculated weight loss.

The discrepancy between the calculated and measured weight losses was not caused by leakage through the cell walls or between the lid and cell body. Leakage should have caused the ratio of the measured/calculated weight losses to decrease with increased orifice area. But no dependance of the ratio on orifice area was observed when the orifice area was varied by a factor of twenty. Furthermore, the discrepancy in the two runs with the graphite cell was of the same order as that measured with the alumina cells.

Undetected vapor species might have caused the discrepancy between measured and calculated weight losses. But, as mentioned above, a run made at 950°C showed no vaporizing species or measurable weight loss. If some new species had appeared at higher temperatures which for some reason escaped detection, a discrepancy would have resulted between the second law heats calculated from the mass spectrometric observations of the $S_2^+$ and $Ga_2S^+$ and the second law heat calculated from torsion effusion measurements of the total pressure. No discrepancy between the heats was found. No gross impurity that could have affected the weight
loss was revealed in the spectroscopic analysis.

The most likely source of the discrepancy is that there is an error either in the temperatures measured in the current study or in the pressures reported by Kashkooli and Munir. Fortunately, when the concordant temperature dependence of the two studies is used in conjunction with the correction for the measured weight loss given below, the effusion rates so determined are accurate no matter which of the two studies is in error. If the effusion rates are accurate, the composition changes calculated would be accurate, although, if the discrepancy arises from an error in temperature measurement in this study, the temperatures reported here for the composition changes could be up to 30 K too low. The conclusion that the magnitude of the composition change is correct is supported by a chemical analysis (see below).

To correct for the discrepancy between measured and calculated weight losses in the composition calculations, all the effusion rates calculated from the intensity data for a given run were multiplied by a constant "\( W \)" where

\[
W = \frac{W_{\text{start}} - W_{\text{end}}}{W_{\text{start}} W_{\text{end}}} 
\]

\( W_{\text{start}} \) = starting weight

\( W_{\text{end}} \) = weight at the end of the run

and "measured and "calculated" have the meanings as given above.

The compositions were then recalculated using the new effusion rates. When the calculations were performed using the \( U_j \) values calculated at
the start of the run for the entire run, this gave results in which the "measured" weight loss exactly equaled the new "calculated" weight loss. When the calculations were performed with different \( U_1 \) values for each group of points calculated by the iterative method, the "calculated" and "measured" weight sometimes did not agree exactly. In this event, a new \( W \) was calculated and the entire calculation repeated until the desired agreement was reached.

The effusion data adjusted by the constant \( W \) to make the "calculated" and "measured" weight losses agree should best minimize errors in calculated pressure versus composition data. The total pressure vs temperature is the average of many measurements so that the requirement that the total pressure at congruency be equal to this average value should give the most consistent and accurate results.

After the pressures and weight loss correction factors had been determined, the composition and pressures of the components at any time could be calculated by linearly interpolating between the measured points. In this way it was possible to map out pressure vs composition curves for each species.

All of the variation in composition for congruent vaporization with temperature results are presented in Figs. 2 and 3. (Note the difference in composition scales between the two figures.) To avoid crowding on the figures, the first point in each run is not plotted, but the range of initial temperatures is represented by the error bar at the assumed starting composition, 59.72 a/oS. The exact starting temperature for each run is given in the legend of the plot. Run 7 is an exception and is discussed below. The numbers next to the points indicate the order
in which they were taken.

The order is important because the errors associated with this experimental method are essentially cumulative. The difference in composition between two successive points is much more accurately determined than the difference between points taken at the start and end of a run. Any error in the composition early in a run is carried over to compositions calculated later in the run.

Another factor that influences the reliability of the data is the amount of sample remaining in the cell. In several runs the sample was almost completely exhausted by the end of the run. Small errors in effusion measurements produce increasingly large errors in calculated composition as the quantity of sample remaining becomes small.

The time needed for the congruent composition to be reestablished after a particular temperature change is a function of both the total sample weight and of the orifice area. Since all these factors are important, a brief summary of each run with special reference to any of the factors that would effect the reliability of any of the points is given. See Table V for the initial and final sample weights.

Run 1

No anomalies.

Run 2

Essentially a repeat of Run 1 but with a larger orifice.

Run 3

Point 2 is probably in error because the sample was thought to have reached the composition of congruent vaporization when in actuality it had not. This error is carried over to points 3 and 4.
Runs 4 and 6

In the two runs, 4 and 6, carried out in graphite cells CS$_2^+$ ion was observed. Thermodynamic calculations indicate that there should be no purely solid state reaction between the cell and sample and none was observed. But the equilibrium constant for the reaction $C(s) + S_2(g) = CS_2(g)$ is greater than 1 for the temperature range examined$^{17}$ Thus most of the $S_2(g)$ should react with the graphite cell. However, unfavorable kinetic factors apparently kept the carbon plus sulfur reaction from reaching equilibrium. The measured $CS_2^+/S_2^+$ ratio reached a maximum of only about 1/3 at the highest temperatures studied.

The formation of $CS_2^+$ in the gas phase probably did not significantly alter the overall gallium sesquisulfide vaporization reaction but, by removing $S_2$ from the vapor, just decreased the $S_2^+$ ion intensities. If the fraction of the $S_2^+$ ion intensity lost by the reaction was fairly constant at any one temperature, much of the error introduced by the $CS_2$ formation should be corrected for in the method used to make the calculations. Since the vapor was assumed, at steady state, to reflect the solid composition, the weighting factors, $U_{S_2}$ and $U_{Ga_2S}$ used to convert ion intensities to pressures, are automatically adjusted if the ion intensities are systematically disturbed. Thus, even if the measured intensities are incorrect, the calculated pressures and effusion rates can be correct.

Despite the uncertainty introduced by $CS_2$ formation, the results of the graphite runs are useful because equilibrium pressure vs composition data at constant temperature were desired. A smaller orifice could be fabricated in the graphite than in the alumina, and the runs with the
small orifice are needed for comparison with the runs with the larger
alumina orifices to determine if equilibrium conditions were approached.

Run 5

No anomalies.

Run 7

This is the only run that was not started at 1270°K. The entire
run was made below the 1230°K transition with a starting temperature of
1210°K. The starting composition was taken as 60.15 a/o S in the calcu-
lations. This composition was determined in a chemical analysis of a
sample annealed at 1210°K (Run 9). The chemical analysis was performed
and evaluated in the same manner as the chemical analysis performed on
the sample which had been annealed at 1270°K.12

The first few points of the run may be slightly in error as a result
of having been taken before congruency had actually been fully estab­
lished. It of course takes much longer for a given composition change
to occur at low temperatures due to the lower effusion rates.

Run 8

Most of the sample had evaporated by the end of the run. This may
have contributed to the apparent error in point 7 which was carried over
to point 8.

Run 9

This run was made primarily to prepare a sample for chemical
analysis and was made with a very large sample which nearly filled the
effusion cell.
Run 10

Point 7, which appears discordant with the other data of Fig. 2, can be understood by reference to Fig. 3. Point 7 was probably taken above what will be interpreted in the discussion as a transition temperature while the composition was changing and does not reflect an equilibrium composition. The final sample weight was very small making the last points, shown on Fig. 3, uncertain.

Run 11

No anomalies.

Run 12

No anomalies.

Run 13

Only one temperature above the temperature of the initial anneal was examined because with the relatively large orifice used, molecular flow conditions may have broken down. This effect is largely corrected for in the iterative type calculations of the composition since the overall effusion rates are adjusted to agree with the total weight losses. This correction is not exact because a small effect of selective scattering from the high pressure molecular beam $^{18}$ may have occurred.

Run 14

Because of temperature control problems, the temperature, when first changed, went above the temperature at which point 2 was recorded. The sample may have started to go through the $1295^\circ$K transition before the temperature was lowered to the desired value. The resultant error probable for point 2 could cause the remaining points to be displaced in the same direction.
Run 15

No anomalies.

The congruent vaporization vs temperature data may be logically divided into three temperature regions: \( T<1230^\circ K \), \( 1230^\circ K<T<1295^\circ K \), and \( T>1295^\circ K \). These regions and the transitions between them are discussed separately.

**\( T<1230^\circ K \)**

The congruent composition changes very little with temperature. It does drift perhaps 0.01 a/o towards a composition richer in sulfur as the temperature is lowered. As \( 1230^\circ K \) is approached, the sample tends to lose more sulfur but the data are rather scattered.

**\( 1230^\circ K \) Transition**

The chemical analyses of samples annealed at \( 1270^\circ K \) and \( 1210^\circ K \) giving 59.72 a/o S and 60.15 a/o S respectively agree very well with the differences in composition calculated from our effusion data. Most of this composition change is due to an abrupt change at \( 1230 \pm 5^\circ K \). This change of \( \sim 0.34 \) a/o S is probably caused by a phase transformation. Three polymorphs of gallium sesquisulfide solid are reported in the literature (see above). X-ray diffraction patterns of samples quenched in the present study from \( 1270^\circ K \) and \( 1210^\circ K \) show the same \( \alpha\text{-Ga}_2\text{S}_3 \) structure.\(^{19}\) But many solid state transitions, for example, the transition between \( \alpha \) and \( \beta \) quartz, cannot be prevented by quenching.\(^{20}\)

Additional evidence of a phase transition was obtained from observations of the \( \text{Ga}_2\text{S}^+ \) intensity of a sample held between \( 1295 \) and \( 1230^\circ K \) when the heating power was turned off. The intensity immediately dropped as expected, but then rose to a maximum before decreasing to zero as the
sample continued to cool. This rather large effect is not due to significant heating of the sample by a latent heat of transition since a similar maximum was not observed when the $S_2^+$ intensity was monitored. The $Ga_2S^+$ maximum may be an indication that the sample's structure has changed on cooling increasing the gallium activity and the $Ga_2S^+$ intensity for a brief time until continued cooling eliminates all vaporization.

$1230^\circ K < T < 1295^\circ K$

This is a single phase region in which the composition for congruent vaporization moved toward the gallium rich side of the diagram by ~0.09 a/o S as the temperature is raised to $1295^\circ K$. Data taken in the region at the start of a run, before any of the transitions were traversed, or taken in runs that were confined solely to this temperature region give the best indication of the way the composition varies with temperature. Points taken after one of the transitions has been traversed, although useful to demonstrate closure of the method, contain rather large errors relative to points taken at the start of a run.

$1295^\circ K$ Transition

This transition occurs when the composition for congruent vaporization reaches the solid-liquid phase boundary. The composition change is an order of magnitude larger than the changes observed at lower temperatures and is accompanied by a correspondingly large uncertainty in the calculated composition. The total vapor pressures are also much larger so any small error in measurement is reflected by a large error in composition. Due to the large composition changes and the high pressures, large amounts of material were effused while a composition change occurred. This large weight loss left a smaller solid sample behind,
further increasing the uncertainty of the measurements. Several points, as is mentioned above in the detailed examination of each run, were taken with such a small amount of sample that their accuracy is extremely low.

The identification of the transition as a solid-liquid phase change is based on the observation that all samples heated above 1295°K appeared to have melted and were firmly stuck to the bottom of the cells. Samples that were not heated above 1295°K, while exhibiting evidence of sintering, maintained a granular character and were easily removed from the cells.

\( T > 1295°K \)

The agreement between compositions recorded when temperatures were raised and when temperatures were lowered show that the samples reached congruently vaporizing conditions. The observation that in this range the samples had melted is in agreement with past determinations of the phase diagram at these temperatures and compositions.

Samples that had come to steady state vaporizing conditions above 1295°K, and were presumably there molten with a composition of \( \approx 57 \text{ a/o S} \), have room temperature X-ray diffraction patterns showing a mixture of \( \text{GaS(s)} \) and \( \text{Ga}_2\text{S}_3 \) phases. These samples showed two maxima of the Ga\(_2\)S\(_4^+\) intensity during rapid cooling while the S\(_2^+\) intensity again merely decreased monotonically.

Pressure vs composition curves were calculated for samples passing through the phase transitions at 1230° and 1295°K and for samples changing composition within the single phase region between 1230°K and 1295°K. The curves represent the pressure-composition paths various
samples followed between two successive congruent vaporization compositions shown in the congruent composition vs temperature plots of Figs. 2 and 3. The numbers of the points corresponding to Figs. 2 and 3 between which the composition change occurred and also the run numbers are given in the pressure versus composition figure captions.

On some figures, points are plotted on the curves while on others only the curve is drawn. This difference has no significance. The pressure vs composition data are derived data so the points just represent interpolated values, not directly measured quantities. The points were only included when it was thought that they would make the drawing easier to read.

The asterisks on the figures represent the final values after steady state was reestablished. The gap between the asterisk and the solid line plotted on the diagram represent a long time when the composition had essentially stabilized but data were still collected to ensure that steady state had been reached. During this long time, fluctuations in temperature and other machine variations sometimes caused what would appear to be fluctuations in pressure at constant composition. Consequently, plotting was suspended during this time.

The time elapsed from the time at which the temperature was abruptly changed to initiate the shift in congruent composition is noted by the arrows at the bottom of the figures. On those figures which record the effect of a temperature increase, the time increases from right to left. This reversal of time scale is used so that compositions of increased sulfur content appear at the right of pressure versus composition plots for heating as well as for cooling.
The temperatures recorded are shown near the bottom of the figures. Pressure vs composition at constant temperature curves were desired but experimentally they were sometimes difficult to obtain. Since the method inherently depends on observing the variation in composition between the congruent vaporization composition at two different temperatures, an initial temperature change, which cannot be accomplished instantaneously, is required. Relative to this point it should be remembered that the temperatures reported are the thermocouple readings and the sample may require a longer time to reach the reported temperature after an abrupt temperature change than does the thermocouple.

It was sometimes difficult to maintain constant temperature over long periods of time. The temperature sometimes drifted slowly, causing what appears to be, if this temperature drift is not taken into account, pressure vs composition curves which would not reflect equilibrium conditions. Occasionally, due to machine difficulties, the temperature took unintended abrupt excursion. These excursions caused many of the apparent irregularities recorded in the pressures.

The attainment of equilibrium is always a problem when dynamic methods are employed to gather thermodynamic data and is especially severe in a study such as this where the composition of the solid is changing and solid state diffusion may limit equilibration.

The equilibrium problem can usually be resolved by varying the orifice area and comparing the results. This was done in the present study but since there were so many variables that affected the form of the pressure vs composition curves, it was difficult to experimentally obtain directly comparable data with different orifices. Consequently,
it was not possible to definitely prove in each case if equilibrium conditions were achieved. The problem is discussed for the various curves in the detailed consideration of the data presented below.

Figures 4 through 9 show pressure vs composition curves for several samples as the 1230°K transition is traversed. All the data were taken after a temperature drop except the data in Fig. 9 which were taken after a temperature increase. Figures 8 and 9 show data taken during the same run. Note that in Fig. 9 the time increases to the left.

Figures 4, 5, and 6 represent runs where the temperature was changed to approximately the same value, 1205°K. They also represent approximately the same sample weights and thus they provide an opportunity to see, by comparing the behavior with different orifice areas, if the curves represent equilibrium pressure vs composition data.

The curves have the same overall shape but there is some difference between the two smaller orifices, Figs. 4 and 6, and the largest orifice, Fig. 5. With the largest orifice, the maximum ratio of Ga$_2$S to S$_2$ recorded was about 9 (Fig. 5). For the next smallest and smallest orifices, which differ in effective areas by about a factor of three, these ratios were 16 and 15 respectively. Because these pressures do not depend on the effective orifice areas, they are shown to be essentially equilibrium values. Table IV gives the pressure ratios and products at other composition.

All the data show, after the initial temperature change has been made, the same behavior with the S$_2$ pressures decreasing and the Ga$_2$S pressures increasing. Over a large fraction of the composition range traversed pressures remain fairly constant, probably because two
condensed phases are at equilibrium. The pressures then change rather abruptly to those of the congruent composition, probably because the stable composition range of a single phase has been reached.

Figures 7 and 8 show similar data for additional runs. The data in Fig. 7 were taken with a large orifice and, in comparison to the other runs, with a very large sample weight. Figure 8 shows data for a sample of approximately the same size and orifice area as Fig. 4; however, the temperature at which steady state was reestablished was about 20 K higher than in Figs. 4, 5, and 6. The change in temperature may account for the lack of the abrupt change in pressures near the steady state value which is seen in Figs. 4, 5, and 6. In Fig. 8 the congruent composition after the transition may be very close to the phase boundary so not much of the single phase region is traversed before the composition stops changing.

Figure 9, taken during the same run as Fig. 8, shows the composition changes that result from a temperature increase. The curves, after the initial jump, show steady linear pressure changes with composition. This is characteristic of pressure changes that occur as a single phase region is traversed.

A schematic phase diagram that can explain this behavior is given in Fig. 10a. Points 1 and 3 represent the composition for congruent vaporization at temperatures T_2 and T_1 respectively. The temperature-composition path followed by the sample is indicated by the arrows. If the sample is initially congruently vaporizing in the single phase region A_2 at the temperature and composition of point 1, and the temperature is rapidly reduced to T_1, the sample moves to point 2 in the two-
phase region, $\text{Al}_1 + \text{Al}_2$. Since this is not the composition for congruent vaporization at $T_1$ the composition shifts until the congruent vaporization composition for $T_1$ is reached at point 3. During the composition change from point 2 to point 3, the sample crosses a two-phase region, $\text{Al}_1 + \text{Al}_2$, then enters a single phase region, $\text{Al}_1$.

The reverse of this heating cycle is observed if the sample is vaporizing congruently at point 3 and the temperature is suddenly increased to $T_2$. The sample follows the path from point 3 to 4 passing through the two-phase region into the single phase region, $\text{Al}_2$. Since this is not the composition for congruent vaporization at temperature $T_2$, the composition shifts to the appropriate congruent composition at point 1. The change from point 4 to 1 is accomplished entirely within the single phase region, $\text{Al}_2$.

Figures 10b and 10c represent partial pressure vs composition curves for $\text{S}_2$ and $\text{Ga}_2\text{S}$ corresponding to the phase diagram in 10a. The solid lines indicate pressure vs composition at $T_2$ while the dashed lines are for $T_1$. The numbers correspond to those of Fig. 10a and the arrows correspond to the path outlined by the arrows of 10a. In reading Figs. 10b and 10c one must keep in mind that, for example, as the temperature is changed from $T_2$ to $T_1$, the pressure shifts, with no change in composition, from the solid to the dashed curve.

In examining Fig. 10b one can see how the increase in the $\text{Ga}_2\text{S}$ partial pressure when the temperature was lowered can be explained. When the temperature is lowered from $T_2$ to $T_1$ the pressure jumps from point 1 to point 2. Then as the composition changes in the two-phase region, the pressure remains constant until the phase boundary is
reached and the pressure starts to decrease until the congruent composition is reached at point 3. When the opposite heating cycle is followed and the temperature is increased from \( T_1 \) to \( T_2 \), the pressure jumps to point 4. Then, as the single phase region is traversed, the pressure steadily increases until the congruent composition is reached at point 1.

One can follow the same path in Fig. 10c for the \( S_2 \) partial pressure which experimentally showed a more expected behavior. During the initial temperature decrease, the pressure decreases from point 1 to 2. As the two-phase region is traversed, the pressure remains constant until the phase boundary is reached and the pressure increases until the congruent composition is reached at point 3. During the reverse heating cycle when the temperature is suddenly increased from \( T_1 \) to \( T_2 \), the pressure jumps from point 3 to 4 then, as the single phase region is traversed, the \( S_2 \) pressure decreases until the congruent vaporization composition is reached at point 1.

Figures 11 through 16 show pressure vs composition data for samples undergoing the 1295°K transition. The composition change here is almost an order of magnitude greater than that of the 1230°K transition. Figures 15 and 16 show data taken after a temperature decrease while the rest of the figures, 11-14, show data taken after a temperature increase.

Similar arguments to those used to explain the data taken during the 1230°K transition can be used to explain the 1295°K transition data. For the 1295°K transition, the situation may be opposite to the 1230°K transition. The data for the 1295°K transition taken after a temperature decrease, Figs. 15 and 16, indicate that the composition changed
completely within a single phase region. The thermodynamically impossible situation shown in Fig. 16 where the Ga$_2$S and S$_2$ pressures both decrease as steady state is approached probably resulted because the quantity of sample was too small to maintain equilibrium. The sample weight after steady state had been reached was only 0.00530 gm.

The data taken after a temperature increase are irregular due to temperature fluctuations and thus are more difficult to interpret. But they may show that initially a two-phase region is crossed followed by a continuing composition change in a single phase region.

Figures 17, 18, and 19 are pressure vs composition plots for the single phase region between 1295°K and 1230°K. The composition changes measured here are much smaller than those that occur during the phase transitions. These very small composition changes are difficult to study because much of the changes can occur before the temperature stabilizes.

To slow the composition change somewhat, samples of about four times the weight used in most of the other runs were used. Even with larger samples, no reliable data could be collected for composition changes initiated by a rise in temperature. Composition changes occur faster at higher temperatures since the total effusion rate is faster.

These curves show that, after the initial drop in temperature was completed, the partial pressures were approximately linear functions of composition as the new congruent composition was approached.

In Fig. 17, the S$_2$ pressure continued to decrease along with the Ga$_2$S pressure. This anomaly appears to be a result of the downward drift in temperature which continued even after the initial temperature drop. During these runs, temperature control proved to be a problem as
is evidenced by the many temperature excursions shown in the figures. However, the changes are those expected for a sample changing composition in a single phase region.
IV. CONCLUSION

The increase of the Ga₂S partial pressure as the temperature decreased has been explained by reference to Fig. 10. Perhaps a simpler way to view the same situation can be found with reference to Fig. 20. Figure 20 shows schematic curves of the free energy of the condensed phase, relative to its formation from Ga₂S(g) and S₂(g), vs composition at two temperatures. T₂ can be viewed as a temperature above the 1230°K transition while T₁ is some temperature below the transition. The solid and dashed curves represent two different solid solutions. The congruent vaporization compositions at temperatures T₂ and T₁ are Xₜ₂ and Xₜ₁ respectively.

At T₂ (Fig. 20a) the partial molal free energy of each component can be found from the intercepts of the tangent. After a temperature change from T₂ to T₁ the composition changes from Xₜ₂ to Xₜ₁ along the free energy-composition path given by 1-2-3-4 in Fig. 20b. For the composition range where the free energy is represented by the common tangent to the two curves, the partial molal free energy and in turn the partial pressure of Ga₂S may be greater than it was under the conditions of Fig. 20a.

Thus, although the increase in Ga₂S pressure is at first intuitively disturbing, when viewed as above, it is seen to be perfectly compatible with the laws of thermodynamics.

To see how the free energy of formation of the solid varied with composition in the region of the 1230°K transition values of ∆G°₁ for the reaction
were calculated from the relation

\[
\left( \frac{1-x}{2} \right) \text{Ga}_2\text{S}(g) + \left( \frac{3x-1}{4} \right) \text{S}_2(g) = \text{Ga}_{1-x}x(S)
\]

were calculated from the relation

\[
\Delta G^0 = RT \ln \left[ \frac{\left( P_{\text{Ga}_2\text{S}} \right)^{\frac{1-x}{2}} \cdot \left( P_{\text{S}_2} \right)^{\frac{3x-1}{2}}} \right]
\]

at various compositions (see Fig. 21) from the partial pressure vs composition data of Figs. 4, 6, 7, 8, and 9. The data from Fig. 5 (Run 2) were not used since the temperature showed a relatively large drift during that run and these free energy vs composition plots are very sensitive to temperature changes.

It should be remembered that the curve in Fig. 21 labeled Run 5 (heating) was calculated from the data in Fig. 9 which were taken after a temperature increase and represent a different phase than do the other curves in Fig. 21. Time increases to the left for the Run 5 (heating) curve. The data taken immediately after the initial temperature change, which show large variations, were not used to calculate the points in Fig. 21.

The curves in Fig. 21 for Runs 1, 4, 5 (cooling), and 9, represent two-phase regions on the gallium rich composition sides and single phase regions on the sulfur rich composition sides. The entire Run 5 (heating) curve represents a single phase region.

Plots of the free energy of formation vs composition at constant temperature should be linear in two-phase regions and show negative curvature in single phase regions. The slight curvatures shown in
Fig. 21 are in the wrong direction except for the curve obtained during cooling in Run 5. Despite this experimental flaw, the curves are useful in that they show the integral free energy is very nearly independent of composition. This result may not be surprising considering the limited composition range, but it is significant when one considers the large changes in the partial quantities, as shown by the partial pressure vs composition plots, which occur as this composition range is traversed.

The relatively small change in integral free energy with composition also supports the contention that the composition shift and even the phase change may be ignored when calculating integral quantities such as the total heat of vaporization.
ACKNOWLEDGMENT

Data and advice provided by David Feather and Alfred Büchler were of great help in this study. David Meschi gave frequent technical help but more importantly was the primary contributor to the non-technical conversations which helped pass many long frustrating days. Alan Searcy who initiated and directed this work deserves my special thanks for his continuing support notwithstanding my several long absences.

This research was supported by the United States Atomic Energy Commission.
REFERENCES


Table I. Orifice Dimensions

<table>
<thead>
<tr>
<th>Orifice</th>
<th>Material</th>
<th>Diameter (cm)</th>
<th>Thickness (cm)</th>
<th>Clausing Factor</th>
<th>Relative Effective Area*</th>
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<td>1</td>
<td>Al₂O₃</td>
<td>0.0406</td>
<td>0.0424</td>
<td>0.5044</td>
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<td>Al₂O₃</td>
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<td>0.0546</td>
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<td>Al₂O₃</td>
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<td>0.1041</td>
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<td>0.2515</td>
<td>0.05</td>
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</table>

* Area x Clausing factor relative to orifice 4.
Table II. Fragmentation Pattern

<table>
<thead>
<tr>
<th>Ion</th>
<th>Present study</th>
<th>Uy et al.</th>
<th>Neutral Precursor</th>
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<td>100.0</td>
<td>S₂</td>
</tr>
<tr>
<td>Ga₂S⁺</td>
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<td>Ga₂S₂</td>
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<tr>
<td>Ga₂O⁺</td>
<td>1.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>Ga₂O (Impurity)</td>
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</table>

<sup>a</sup> Relative intensity increases with temperature. The value given here is the relative value at 1370°K.

<sup>b</sup> This is the maximum value found in the as received sample. The intensity decreased with the fraction of the sample vaporized.
Table III. Data used to calculate $\Delta H$ for the reaction $\text{Ga}_2\text{S}_3(\text{s}) = \text{Ga}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$

<table>
<thead>
<tr>
<th>Temperature $^a_{^o\text{K}}$</th>
<th>Intensity $^b$</th>
<th>Weighting factor $^c$</th>
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<tr>
<td></td>
<td>$\text{S}_2^+$</td>
<td>$\text{Ga}_2\text{S}^+$</td>
</tr>
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<td>1281</td>
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<tr>
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<td>1192</td>
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<td>1207</td>
<td>10.35</td>
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$^a$ These temperatures have been corrected by adding 12°K to the measured values.

$^b$ These intensities have not been corrected for isotopic abundance and are the measured intensities of the isotopes of $\text{S}_2$ and $\text{Ga}_2\text{S}$ at mass numbers 64 and 172 respectively.

$^c$ The $[I_1^+ I_2^+ T^2_2^+]$ data were multiplied by this factor to form the "combined" data.
Table IV. Enthalpies calculated from the data of Table III

<table>
<thead>
<tr>
<th>Orifice</th>
<th>Temperature range °K</th>
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<th>$\Delta H$ calculated from the slope of log [ ] vs 1/T Kcal</th>
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<td>$[I_{S_2}^+] T$</td>
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<tr>
<td>1</td>
<td>1286-1114</td>
<td>1200</td>
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<td>3</td>
<td>1207-1050</td>
<td>1128</td>
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<td>Combined data</td>
<td>1286-1050</td>
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<td>-</td>
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Table V. Measured and calculated\textsuperscript{a} sample weights

<table>
<thead>
<tr>
<th>Run</th>
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<th>Temp. range °K</th>
<th>Measured weight gm</th>
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<td>6</td>
<td>G</td>
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\textsuperscript{a} See text for explanation of "measured" and "calculated".

\textsuperscript{b} \( W = \frac{\text{measured weight loss}}{\text{calculated weight loss}} \)
Table VI. Pressure ratios\(^a\) and products\(^b\) from the data in figures 4, 5, and 6

<table>
<thead>
<tr>
<th>Composition a/o S</th>
<th>Run 1(^c) Figure 4</th>
<th>Run 2(^d) Figure 5</th>
<th>Run 4(^e) Figure 6</th>
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<tbody>
<tr>
<td></td>
<td>Temp (^o)K</td>
<td>Ratio(^a)</td>
<td>Product (x10^{10}) (atm(^2))</td>
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<tr>
<td>59.80</td>
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<td>59.85</td>
<td>1205.0</td>
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<td>1205.0</td>
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<td>0.78</td>
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\(^a\) Ratio = \(P_{Ga_2S}/P_{S_2}\)

\(^b\) Product = \(P_{Ga_2S} \cdot P_{S_2}\)

\(^c\) Alumina orifice, effective area = \(0.653 \times 10^{-3}\) cm\(^2\).

\(^d\) Alumina orifice, effective area = \(4.087 \times 10^{-3}\) cm\(^2\).

\(^e\) Graphite orifice, effective area = \(0.197 \times 10^{-3}\) cm\(^2\).
FIGURE CAPTIONS

Fig. 1. Ion intensity (Ga$_2$S$_4^+$ and S$_2^+$) vs time for Run 4 orifice G. The intensities are corrected only for isotopic abundance.

Fig. 2. Congruent vaporization composition vs temperature below 1295°K.

Fig. 3. Congruent vaporization composition vs temperature for samples passing through the 1295°K transition. Run 10 is included for ease in comparing the composition scales of Figs. 2 and 3.

Fig. 4. Partial pressure vs composition from Run 1 (orifice 1). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 5. Partial pressure vs composition from Run 2 (orifice 4). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 6. Partial pressure vs composition from Run 4 (orifice G). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 7. Partial pressure vs composition from Run 9 (orifice 4). The congruent composition change follows a temperature decrease and is from point 1 to 2 of Fig. 2. As is seen from Table V, a large sample was used (0.76 gm).

Fig. 8. Partial pressure vs composition from Run 5 (orifice 1). The congruent composition change follows a temperature decrease and is from point 3 to 4 of Fig. 2.
Fig. 9. Partial pressure vs composition from Run 5 (orifice 1). The congruent composition change follows a temperature increase and is from point 9 to 10 of Fig. 2.

Fig. 10. (a) Schematic phase diagram.
(b) Partial pressure of Ga$_2$S vs composition corresponding to the phase diagram in 10a.
(c) Partial pressure of S$_2$ vs composition corresponding to the phase diagram in 10a.

Fig. 11. Partial pressure vs composition from Run 6 (orifice G). The congruent composition change follows a temperature increase and is from point 2 to 3 of Fig. 3.

Fig. 12. Partial pressure vs composition from Run 10 (orifice 1). The congruent composition change follows a temperature increase and is from point 7 to 8 of Fig. 3.

Fig. 13. Partial pressure vs composition from Run 11 (orifice 1). The congruent composition change follows a temperature increase and is from point 2 to 3 of Fig. 3.

Fig. 14. Partial pressure vs composition from Run 13 (orifice 3). The congruent composition change follows a temperature increase and is from point 1 to 2 of Fig. 3.

Fig. 15. Partial pressure vs composition from Run 6 (orifice G). The congruent composition change follows a temperature decrease and is from point 4 to 5 of Fig. 3.

Fig. 16. Partial pressure vs composition from Run 10 (orifice 1). The congruent composition change follows a temperature decrease and is from point 9 to 10 of Fig. 3.
Fig. 17. Partial pressure vs composition from Run 12 (orifice 1). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 18. Partial pressure vs composition from Run 14 (orifice 1). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 19. Partial pressure vs composition from Run 15 (orifice 1). The congruent composition change follows a temperature decrease and is from point 2 to 3 of Fig. 2.

Fig. 20. Schematic free energy vs composition diagram for the formation of the condensed phase from $\text{Ga}_2\text{S}_3(\text{g})$ and $\text{S}_2(\text{g})$.

Fig. 21. Free energy of formation of gallium sesquisulfide from $\text{S}_2(\text{g})$ and $\text{Ga}_2\text{S}_3(\text{g})$ vs composition. Values for Runs 1, 4, 9, 5 (decreasing), and 5 (increasing) were calculated from the data in Figs. 4, 6, 7, 8, and 9 respectively.
Figure 1
Figure 2
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 13
Figure 14
Figure 15
Figure 16
Figure 17
Figure 18
Figure 19
Figure 20
Figure 21
C PROGRAM TO CALCULATE PRESSURES AND SOLID COMPOSITIONS
C FROM INTENSITY, TIME, TEMPERATURE DATA
LARGE TM(300,20,2), TC(300,20,2), V(300,20,2), EM(300,20,2),
* TK(300,20,2), VTK(300,20,2), P(300,20,2), EM(300,20,2),
* EGI(300,20,2), E(300,20,2)
DIMENSION R(2), GFW(2), WW(2C,2), PEAK(2), EMT(20,2), EGT(20,2), JB(2)
DIMENSION WM(20,2), GATT(2C), GAT(2C,2), GATS(20,2), APCS(2,2)
DIMENSION APC(20,2), WTLS(20)
DIMENSION TKF(20,2), TSF(20,2), VF(20,2), FVR(20)
DIMENSION EGT(20), EGTT(20), EGTT(20,2), EMTW(20,2)
DIMENSION NN(20,2), KN(2C), GLWT(20), TSW(20)
LARGE TSWK(300,20)
DIMENSION TSW(300,20,2), TIME(300,20,2), PRES(300,20,2), LMA(300,20,2),
* TMATK(300,20,2), RMAK(300,20,2), RMAK(300,20,2), APMATK(300,20,2)
DIMENSION EQLI(300,20,2)
DIMENSION TEMPK(300,20,2), DFL(300,20,2), DF(300,20,2)
DIMENSION PMUNI(20), XF(100), X(20,100)
DIMENSION WWW(11C)
REAL MOLWT, MS2, MGA2S
REAL MS, MGA
DATA PEAK(1)/5H 52, PEAK(2)/5H GA2S/
MS2 = 64.128
MGA2S = 171.504
MS = 32.264
MGA = 69.12
GASR = 1.98726
R(1) = SQRT(MGA2S/MS2)
R(2) = SQRT(MS2/MGA2S)
GFW(1) = MS2
GFW(2) = MGA2S
C RUN IDENTIFICATION
51 READ 16, (WORD(L), L=1,12)
16 FORMAT(12A6)
PRINT 17, (WORD(L), L=1,12)
17 FORMAT(1H1,12A6)
C D=ORIFICE DIAMETER IN CM
C C=CLAUSING FACTOR
READ 204, D, C
204 FORMAT(2F10.7)
C AO = ORIFICE AREA IN CM**2
AO = (D/2)**2*3.1416
PRINT 305, D, AO, C
305 FORMAT(1DHOURIFICE DIAM CM = ,F9.7,21H ORIFICE AREA CM = ,E13.7, *
*2H CLAUSING FACTOR = ,F10.7)
JB(1) = 0
JB(2) = 0
C THE DATA ARE READ IN GROUPS INDEXED BY J
C THE GROUPS INCLUDE DATA TAKEN BETWEEN SUCCESSIVE TEMPERATURE CHANGES
C ALL THE N POINTS OF ONE SPECIES,L,(L=1 FOR S2,L=2 FOR GA2S) OF ONE
C GROUP,J, ARE READ SUCCESSIVELY IN THE ORDER THEY WERE MEASURED
C ALL OF THE GROUPS OF ONE SPECIES NEED NOT BE READ CONSECUTIVELY
50 READ 205, L, N
FORMAT(I2,I8)
IF (N .EQ. 0) GO TO 803
JJ(L) = JB(L)+1
J = JB(L)
NN(J,L) = N
JJ = J
C TM=TIME IN MINUTES FROM THE START OF THE EXPERIMENT
C TC=TEMPERATURE IN DEGREES C AS READ FROM THE THERMOCOUPLE
C V=ION INTENSITY
READ 200,(TM(I,J,L), TC(I,J,L), V(I,J,L), I=1,N)
20: FORMAT (2F10.3,F13.5)
GO TO 50
803 CONTINUE
C LVOUT WAS ALWAYS = 2
C WT=SAMPLE WEIGHT MEASURED BY WEIGHING AT THE START OF THE RUN
C WTEND=SAMPLE WEIGHT MEASURED BY WEIGHING AT THE END OF THE RUN
READ 750,LVOUT,WT,WTEND
750 FORMAT(12,F8.5,F10.5)
PRINT 300
300 FORMAT(96HOPEAK GP. PT. TIME(MIN) TIME(SEC) TEMP(C)
* TEMP(K) INTENSITY INTENSITY*T(K))
DO 800 L = 1,2
DO 811 J=1,JJ
N = NN(J,L)
DO 1 I=1,N
C THIS CORRECTS THE INTENSITIES FOR ISOTOPIC ABUNDANCE
IF(L .EQ. 1) V(I,J,L) = VI(J,L)/0.902614
IF(L .EQ. 2) V(I,J,L) = VI(J,L)/0.4698735
C TS= TIME IN SECONDS
TS(I,J,L) = TM(I,J,L)*60.
C CONVERT TO KELVIN AND MAKE TEMPERATURE CORRECTION
TK(I,J,L) = TC(I,J,L) + 273.15
VTK(I,J,L) = VI(J,L)*TK(I,J,L)
1 CONTINUE
TKF(J,L) = TK(N,J,L)
TSF(J,L) = TS(N,J,L)
VF(J,L) = VI(N,J,L)
PRINT 302,(PEAK(L),J,1,TM(I,J,L),TS(I,J,L),TC(I,J,L),TK(I,J,L),
* VI(J,L),VTK(I,J,L), I=1,N)
PRINT 612
800 CONTINUE
C START COMPOSITION AND PRESSURE CALCULATION
PRINT 17,(WORD(L),L=1,12)
WWW(I) = 1.
K=1
92 CONTINUE
4 FORMAT( F87.6)
C W=WEIGHT LOSS CORRECTION FACTOR
W = WWW(KK)
DO 808 J=1,JJ
LL = 0
807 CONTINUE
LL = LL + 1
C X=MOLE FRACTION OF SULFUR IN THE SOLID
X(J,L) = (.5972
DO 806 L=1,2
N=NN(J,L)
C PMUNIR=TOTAL PRESSURE OVER GA2S3 MEASURED BY TORSION EFFUSION BY MUNIR
PMUNIR(J) = PMUNIR(J)/(VT(N,J,L)*(1.+L/BRAK))
BRAK = (3.*X(J,LL)-1.)/(1.*X(J,LL))
XF(J) = X(J,LL)
IF ( L EQ. 2) GO TO 804
C WW=WEIGHTING FACTOR TO CONVERT INTENSITY*TEMP DATA TO PRESSURES,P
WW(J,L) = PMUNIR(J)/(VT(N,J,L)*(1.+L/BRAK))
C PUT IN WW(J,L)=WW(1,L) TO KEEP WEIGHTING FACTORS CONSTANT
GO TO 805
804 WW(J,L) = PMUNIR(J)/(VT(N,J,L)*(1.+L/BRAK))
3) CONTINUE
EMT(J,L) = 0.
FGT(J,L) = 0.
EM(I,J,L) = 0.
EG(I,J,L) = 0.
TEM(I,J,L) = 0.
DO 2 I=1,N
P(I,J,L) = VTK(I,J,L) * WW(J,L)
C CALCULATE EFFUSION RATE IN MOLES AND GRAMS/SECOND
ZM(I,J,L) = P(I,J,L)*AO*(44.3305722 / SQRT(GFWL)*TK(I,J,L))
ZG(I,J,L) = ZM(I,J,L) * GFWL
IF (I*EQ. 1) GO TO 2
EM(I,J,L) = (ZM(I,J,L)+ZM(I-1,J,L))/2.*(TS(I,J,L)-TS(I-1,J,L))
EG(I,J,L) = EM(I,J,L) / GFWL
C CALCULATE THE TOTAL MOLES AND GRAMS OF EACH SPECIES EFFUSED IN GROUP J
EMT(J,L) = EMT(J,L) + EM(I,J,L)
EGT(J,L) = EGT(J,L) + EG(I,J,L)
TEMP(I,J,L) = EMT(J,L)
2 CONTINUE
806 CONTINUE
611 FORMAT(130H0*******************************************************************
612 FORMAT(1HK)
EMT(J,1) = EMT(J,1)*W
EMT(J,2) = EMT(J,2)*W
FBT(J,1) = GFT(J,1)*W
FBT(J,2) = GFT(J,2)*W
FBTT(J) = GBT(J,1) + GBT(J,2)
FBTTT = GBTT(J)
IF (J GT. 1) FBTTT(J) = FBTTT(J-1) + FBTTT(J)
33 FVR(J) = VF(J,1)/VF(J,2)
C SUBTRACT THE WEIGHT EFFUSED WHILE INITIALLY HEATING TO STEADY STATE
GATTS(1) = (HT- (EMTW(1,1)*MS2 + EMTW(1,2)*MGA2S)) / *(MS * X(1,1) + MGA * (1.-X(1,1)))
IFIJ GT. 1) GATTS(J) = GAT(J-1,1) + GAT(J-1,2)
C CONVERT MOLECULAR LOSSES TO ATOMIC LOSSES
GATS(1,1)=GATTS(1)*X(1,1)+2.*EMTW(1,1)+EMTW(1,2)
GATS(1,2)=GATTS(1)*X(1,1)+2.*EMTW(1,2)
27 DO 19 L=1,2
IFIJ GT. 1) GATS(J,L) = GAT(J-1,L)
APCS(J,L) = GATS(J,L)/GATTS(J)*100.
GAT(J,L) = GATS(J,L) - EMTW(J,L)*2. - (2-L)*EMTW(J,2)
19 CONTINUE
GAT(J) = GAT(J,1) + GAT(J,2)
C CALCULATE SOLID COMPOSITION
APC(J,1) = GAT(J,1)/GATT(J)*100.
APC(J,2) = GAT(J,2)/GATT(J)*100.
X(J,L+1) = APC(J,1)*100.
WGT(J) = GAT(J,1)*32.064 + GAT(J,2)*69.71.0
WTLOS(J) = WT - WGT(J)
IF(J .EQ. 1) GO TO 808
TEST = ABS(X(J,LL) - X(J,LL+1))
C ITERATE IF X USED TO CALCULATE WW AT THE START IS NOT RECALCULATED
IF(TEST .GE. .00001 .AND. LL .LT. 4) GO TO 807
808 CONTINUE
PRINT 2021, W
2021 FORMAT(29HOWT. LOSS CORRECTION FACTOR =,F7.4)
PRINT 600
600 FORMAT(93HGP. TIMF(S) TEMP K. PMUNIR ATM WW (S2) WW (GA2S)
* MOL GA25/GP MOL GA25/GP MOL GP TOT GM)
PRINT 601, J, TSF(J,1), TKF(J,1), PMUNIR(J), WW(J,1), WW(J,2),
*EMTW(J,1), EMTW(J,2), EGT(T(J), EGT(T(J), J=1,JJ)
601 FORMAT(I6, F9.1, F9.1, F12.4, 3E11.3, E12.3, 2F8.5)
PRINT 78
PRINT 4, WT
78 FORMAT(97HGP. TIMF(S) TEMP K SV/GA2S START$ S STARTS$GA LAST
* X END $ S END $ GA SAMPLE GM GM LOST)
PRINT 77, J, TSF(J,2), TKF(J,2), FVR(J), APC(J,1), APC(J,2), XF(J),
*APC(J,1), APC(J,2), WGT(J), WTLOS(J), J=1,JJ)
77 FORMAT(I3, F9.1, F9.1, F9.1, F9.1, F10.5, F10.5, 2F10.5, 2F10.6)
KK = KK+1
C CALCULATE WEIGHT LOSS CORRECTION FACTOR
WWW(KK) = (WT-WTEND)/(WT-WGT(JJ))*WWW(KK-1)
TEST2 = ABS(WTEND-WGT(JJ))
PRINT 611
C ITERATE IF CALCULATED AND MEASURED WEIGHT LOSSES DO NOT AGREE
IF(TEST2 .GT. .00001 .AND. KK .LT. 4) GO TO 92
PRINT 17, (WORD(L), L=1, 12)
C PRINT PRESSURES AND EFFUSION RATES CALCULATED FROM INTENSITIES
PRINT 301
301 FORMAT(114HPEAK GP. PT. TIME(MIN) TIME(SEC) PRES. (ATM.)
* Z(MOLE/SEC) Z(GM/SEC) MOL PT TO PT GM PT TO PT)
DO 304 L=1,2
DO 309 J=1,JJ
N=NN(J,L)
PRINT 303, PEAK(L), J, TM(I,J,L), TS(I,J,L), P(I,J,L), ZM(I,J,L),
*ZG(I,J,L), EM(I,J,L), EG(I,J,L), I=1,N)
303 FORMAT(A6, I3, I5, I8, 15, F12.3, F14.3, 5E15.5)
PRINT 612
309 CONTINUE
304 CONTINUE
C THE REMAINING SECTION OF THE PROGRAM INTERPOLATES BETWEEN THE
C MEASURED POINTS TO CALCULATE PRESSURES AND COMPOSITIONS AT SPECIFIC
C TIME INTERVALS SO PRESSURE VS COMPOSITION CURVES CAN BE CONSTRUCTED
C SEC=TIME INTERVAL BETWEEN INTERPOLATED POINTS
C SEC WAS VARIED TO FIT THE NEEDS OF A PARTICULAR SET OF DATA
SEC = 100C.
KEND = 300
DO 2005 J=1, JJ
DO 2005 L=1, 2
N= NN(J+L)
KEND = K(J-1)
I = 1
TIME(I,J) = TS(I,J,L)
K = 1
GO TO 2004
2003 K = K+1
TIME(K,J) = TIME(K-1,J) + SEC
2004 IF(K .EQ. 2 .AND. J .GE. 1) TIME(K,J) = TIME(KEND-L,J-1) + SEC
IF(TIME(K,J) .GE. TS(N,J,L)) GO TO 2002
2006 IF(TIME(K,J) .GE. TS(I,J,L) .AND. TIME(K,J) .LT. TS(I+1,J,L)) GO TO 2001
I = I + 1
GO TO 2006
2002 TIME(K,J) = TS(N,J,L)
I = N - 1
2001 DIVIS = TS(I+1,J,L) - TS(I,J,L)
TEMPK(K,J,L) = TIME(I+1,J,L) - TIME(K,J)) / DIVIS +
* TIME(I+1,J,L) - TIME(K,J)) / DIVIS
PRES(K,J,L) = PRE(I,J,L) * (TIME(I+1,J,L) - TIME(K,J)) / DIVIS +
* TIME(I+1,J,L) - TIME(K,J)) / DIVIS
ZMATK(K,J,L) = -ASR * TEMPK(K,J,L) * ALOG(PRES(K,J,L))
2003 TIME(K,J) = TIME(K,J) - TS(I,J,L)
* TIME(K,J) - TS(I,J,L)
* TIME(K,J) - TS(I,J,L)
IIF(TIME(K,J) .NE. TS(N,J,L)) GO TO 2003
2005 KN(J) = K
SWT = WT
DO 502 J=1, JJ
GAT(I,2) = GATS(I,2)
GAT(I,1) = GATS(I,1)
503 KEND = KN(J)
DO 501 K=1, KEND
FOIL(K,J) = PRE(K,J,1) * PRE(K,J,2)
OF(K,J) = ASR * TEMPK(K,J,1) * ALOG(EQIL(K,J))
RZMK(K,J) = ZMATK(K,J,1) / ZMATK(K,J,2)
RGATK(K,J,1) = GAT(J,1) - RZMK(K,J,1) / RZMK(K,J,2)
RGATK(K,J,2) = GAT(J,2) - RZMK(K,J,2) / RZMK(K,J,1)
TSWK(K,J) = RZMK(K,J,1) * 32.064 * RGATK(K,J,2) * 69.720
DO 501 L=1, 2
501 APATK(K,J,L) = (RGATK(K,J,L)/RGATK(K,J,1) + RGATK(K,J,2)) * 100.
KEND
GAT(J+1,1) = RGATK(K,J,1)
GAT(J+1,2) = RGATK(K,J,2)
GLWTK(J) = (TMATK(K,J,L)) * MS2 + TMATK(K,J,2) * MGA2S * W
SWT = SWT - GLWTK(J)
TSW(J) = SWT
502 CONTINUE
PRINT 17, WORD(L), L=1, 12
PRINT 505
505 FORMAT(119HOGP, TIME(SEC) P S2 (ATM) P GA2S (ATM) AT $ S
  * AT $ GA Z S2(M/SEC) Z GA2S(M/SEC) ZS2/ZA2S TOT WT GM)
  DO 507 J=1, JJ
  KNN = KN(J)
  PRINT 506, (J,TIME(K,J),PRES(K,J,1),PRES(K,J,2),APATK(K,J,1),
  *APATK(K,J,2),ZMATK(K,J,1),ZMATK(K,J,2),RZMK(K,J),TSWTK(K,J),
  *K=1,KNN)
506 FORMAT(I3, F11.1, 2E14.4, 2F13.6,2E14.5, F11.6, F12.6)
  PRINT 612
507 CONTINUE
  PRINT 17,(WORD(L),L=1,12)
  PRINT 2010
2010 FORMAT(129HOGP TIME(S) TK S2 TK GA2S P S2 (ATM) P GA2S ATM
  * PS2*PGA2S. AT $ S AT $ GA -RT*LN(PS2) -RT*LN(PGA2S) -RT*LN(PS
  *2*PGA2S))
  DO 508 J=1, JJ
  KNN=KN(J)
  PRINT 2011, (J,TIME(K,J),TEMPK(K,J,1),TEMPK(K,J,2),PRES(K,J,1),
  *PRES(K,J,2),EQIL(K,J),APATK(K,J,1),APATK(K,J,2),DFL(K,J,1),
  *DFL(K,J,2),DFK(K,J),K=1,KNN)
2011 FORMAT(13, F9.1, 2F9.2, 3E12.4, 2F9.4, 3F13.4)
  PRINT 612
508 CONTINUE
509 READ 2020,N
2020 FORMAT(110)
  IF ( N .LT. 0) GO TO 51
3 CONTINUE
  STOP
  END
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