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THERMODYNAMICS OF THE POTASSIUM-SULFUR-OXYGEN AND RELATED SYSTEMS

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ABSTRACT

The vaporization behavior of K_2S, K_2SO_3 and $K_2S_2O_5$ were studied by Knudsen-cell mass spectrometry and by the simultaneous Knudsen-torsion effusion method, the first in the range 750-950°C, the second in 700-950°C, and the third in 150-400°C. Vaporization reactions of $K_2S_2O_5$(s) and K_2SO_3(s) were nonreversible under conditions within a Knudsen cell. $K_2S_2O_5$(s) gave K_2SO_3(s) and SO_2(g). In a Pt crucible, K_2SO_3(s) gave K_2SO_4(s), K(g), and SO_2(g); in a graphite crucible, it gave S_2(g) instead of SO_2(g). Contrary to previous reports, K_2S vaporizes incongruently to produce principally K(g) and KS_x(l). Crucibles of bulk- and surface-densified graphite and of alumina did not react with K_2S, but some time after the start of each experiment with these crucibles, K(g) began to diffuse through the crucible walls. Experiments in graphite crucibles gave ΔH°(298 K) of K_2S(s), -364±12 kJ/mol and in alumina, -376±12 kJ/mol; values of this quantity given in the literature range from -365 to -406 kJ/mol.

PREFACE

This research was initiated as part of a program sponsored by the Department of Energy and contracted to the National Aeronautics and Space Administration to improve the anticipated K_2CO_3 seed recovery in coal-fired magnetohydrodynamic plasmas. The problem was that chemical reaction of the K_2CO_3 seed with SO_2 from sulfur in the coal would produce K_2SO_4 from which K_2CO_3 was expensive to recover. The objective of the program was to recover part of the potassium as K_2SO_3 or K_2S, either of which could be converted to K_2CO_3 cheaply. Our purpose was to learn the chemical and vaporization behavior and the thermodynamic properties of K_2S and K_2SO_3 by effusion methods including Knudsen-cell mass spectrometry and the simultaneous Knudsen- and torsion-effusion method.

Ours was one of three groups involved in this research. The other two were at the NASA Lewis Research Center (LRC) under the direction of Carl Stearns and Fred Kohl and at Arkansas State University (ASU) under the direction of James Edward Bennett. The principal tools at LRC were a Knudsen-cell mass spectrometer and excellent dry boxes along with an analysis laboratory. The principal tool at ASU was a vacuum microbalance, Knudsen-effusion apparatus with a temperature-regulated vacuum furnace. Initially our principal tool was a computer-automated, simultaneous-Knudsen-torsion effusion apparatus with vacuum furnace. Later, NASA LRC donated to our laboratory a stainless steel, evacuable, dry box, which became one of our most important tools. Still later, the General Electric Company at Nela Park in Cleveland, Ohio donated to our laboratory a Nuclide 12-90 HT Knudsen-cell mass spectrometer which we used with effect toward the end of this research.

I, the principal investigator in our research, gratefully acknowledge the contributions of those in my laboratory who have worked with me on this research. Those include Francois Sibiende, Vyankotesh Chincholkar, Larry Grimes,

Ned Balzer, and Mark Williamson. In addition, I thank our machinist Guenther Buenning and my colleague Bradford Thompson for many valuable contributions. We all are indebted to the personnel at LRC, particularly Carl Stearns, Fred Kohl, Reza Haque, George Fryburg , Joseph Springer, and Warren Phillip for assistance with experiments, discussions, suggestions, and of course for the financial support which made this work possible. The help of people at LRC in our receiving the donations of the dry box, the mass spectrometer, and other experimental equipment is much appreciated. We also thank J. Edward Bennett of ASU whose suggestions and experimental results influenced and guided much of our work.

SUMMARY

This study was initiated to deduce the chemical reactions which occur when potassium sulfide, K_2S, and potassium sulfite, K_2SO_3, are heated at temperatures where their vapor pressures are significant, then to measure the vapor pressures and the partial pressures of the chemical products. The objective was to deduce conditions necessary in MHD flames in order to promote condensation $K_2S(s)$ and $K_2SO_3(s)$ rather than K_2SO_4, either of the former two allowing more economical reconversion to K_2CO_3, the seed material for the MHD plasma.

Pure $K_2S(s)$ was prepared by combination of the elements in a controlled-atmosphere box. A search was conducted for a suitable container material for heating K_2S in the temperature range 750-950°C. Materials unsuitable due to reaction with K_2S were Inconel, nickel, rhenium, platinum, tungsten, and titanium boride. Materials which did not react with K_2S were graphite, aluminum oxide, and zirconium oxide.

Mass spectrometry of the vapor of potassium sulfide revealed only K(g). X-ray studies of the solid residues from vaporization experiments revealed that $K_2S_2(s)$ grew in. Chemical analyses of the same solid residues showed that the residues approached a composition K_2S_x with x in the range 3-4.

Vapor pressure of K_2S was measured by simultaneous Knudsen-effusion and torsion-effusion (SKETE) in crucibles of aluminum oxide and of graphite. In each such experiment the vapor pressures by Knudsen-effusion and by torsion-effusion agreed initially, but then the apparent pressure by Knudsen-effusion increased suddenly and remained much greater than that by torsion-effusion for the remainder of the experiment. This phenomenon was due to the fact that K(g) in the vapor diffused through the walls of the crucibles and presently began to evaporate from the outside of the crucibles. Agreement among the experiments in graphite and aluminum oxide was good in each case until the onset of the high Knudsen pressures.

One of the experiments in high-density graphite could be interpreted on the basis that the extraneous vaporization of K(g) from the exterior of the cell was uniform and symmetric and did not affect the pressure measured by torsion effusion. The results indicated that the vaporization reactions were

$$2/3\ K_2S(s) = 1/6\ K_2S_4(l) + K(g)$$

$$1/4\ K_2S_4(l) = 1/2\ K(g) + 1/2\ S_2(g).$$

Third-law analysis of the torsion pressures gave $\Delta H°(298K)$ of the first reaction, 223.4 ± 0.4 kJ, and of the second reaction, 271.5 ± 0.2 kJ. These results implied a $\Delta H°(298K)$ of formation of $K_2S(s)$ of -364 ± 12 kJ/mol. Measurements reported in the literature of the latter value by a variety of methods range from -365 to -406 kJ/mol.

Pure $K_2SO_3(s)$ was prepared by decomposition of dry $K_2S_2O_5(s)$ in vacuum. In no case was a hydrate of K_2SO_3 found. Some materials identified by others in the past as a hydrate of K_2SO_3 contained no water, commercial suppliers of K_2SO_3 erroneously label it "$K_2SO_3 \cdot 2H_2O$". It is unlikely that a stable hydrate exists.

Because of its relationship to the preparation of K_2SO_3, the vapor pressure of SO_2 during decomposition of $K_2S_2O_5$ was measured by simultaneous Knudsen and torsion-effusion and by mass spectrometry in graphite crucibles.

Platinum and aluminum oxide were shown to be suitable crucible materials for heating $K_2SO_3(s)$ for vaporization in the range 700-950°C. Vapor pressures over $K_2SO_3(s)$ were measured by simultaneous Knudsen and torsion-effusion in a platinum crucible and by mass spectrometry in an aluminum oxide crucible.

The vapor pressures of both $K_2S_2O_5(s)$ and $K_2SO_3(s)$ were nonreproducible at a given temperature. The lack of reproducibility was due to the vaporization reactions of the materials being irreversible under conditions in effusion cells.

A mass spectrometric study of vaporization of K_2SO_3 in a graphite crucible revealed S_2 and K_2S_x with x from 1 to 3 in the vapor. Reduction of the sample by graphite was speculated as a cause for the presence of these species.

INTRODUCTION

When the proposal for this project was written, several aspects of the high-temperature behavior of K_2S had been studied. Its vaporization had been studied twice by mass spectrometry. Bennett, et al.[1] had observed the mass spectrum of vapor from commercial samples of K_2S heated in a Knudsen cell made of molybdenum and another consisting of an alumina liner in a tantalum cell. Ortman[2] had studied by mass spectrometry the vapor of K_2S heated in a rhenium crucible; in that study the K_2S had been prepared from the elements by the method of Dworkin and Bredig.[3] In both investigations the conclusion was that the principal vaporization reaction was represented by

$$K_2S(s) = 2K(g) + 1/2\ S_2(g) \qquad (1)$$

The K-K_2S temperature-composition phase diagram, including the melting point of pure K_2S, had been determined by Dworkin and Bredig[3] by thermal analysis with the samples contained in Inconel capsules. The melting points of the polysulfides K_2S_3, K_2S_4, K_2S_5, and K_2S_6 had been measured[4,5,6] and that of K_2S_2 had been measured.[5] These results could be combined into the temperature-composition phase diagram shown in Figure 1, in which the most recently determined melting points are used.

Because of the amount of work which had been published, the proposal for this project was optimistic that the vapor pressure and vapor composition of $K_2S(s)$ could be measured as a function of temperature. One of the previously used container materials would be suitable to contain vaporizing $K_2S(s)$, the vaporization reaction could be confirmed, and the thermodynamics of vaporization of $K_2S(s)$ could be measured and calculated via the vapor pressures.

This report will show that a great deal was learned about the chemistry and vaporization of $K_2S(s)$ during this project. Reliable vapor pressures were measured, and with the understanding that the proposed vaporization reaction was tentative, the enthalpy of vaporization was measured. However, no suitable container was found for $K_2S(s)$ above 1000°K, where its vapor pressure is measureable, the fact which accounts for the uncertainty about the vaporization reaction.

STUDIES WITH CERAC K_2S

Cerac, Inc., Milwaukee, Wisconsin supplied $K_2S(s)$ prepared by reaction of sulfur with potassium dissolved in liquid ammonia. The $K_2S(s)$ was received in sealed glass vials with argon atmospheres. Cerac analyzed their samples by X-ray powder diffraction and by chemical analysis for sulfur only. They reported that the batch sold to us contained 25% sulfur; theoretical sulfur content of $K_2S(s)$ is 29.1%. They reported that the X-ray powder diffractogram was that of $K_2S(s)$.

In our laboratory the K_2S samples were opened and handled in a nitrogen-filled drybox with P_2O_5 desiccant. Storage of the samples, when they were not being handled, was in the drybox in a vacuum-desiccator over Na/K alloy. Samples placed in Knudsen cells were protected during transfer through the atmosphere to a vacuum system by sealing the orifice with naphthalene.

X-ray powder diffractograms of Cerac $K_2S(s)$ done in our laboratory contained the lines of K_2S and a few, faint, unidentified lines which came to be known among us as the "extra lines". (Later, these lines, inherent to the Cerac samples, were shown to be associated with exposure of samples to the atmosphere.)

Chemical analyses of Cerac K_2S were done by the analytical laboratory at the Lewis Research Center. One analysis for both K and S gave 50% K and 27.2% S by weight. Another, with two aliquots, gave 64.1% and 63.7% K, or an average of 63.9% K; no sulfur analysis was done. Another, with two aliquots, gave 64.8% and 62.9% K, or an average of 63.8% K; no sulfur analysis was done. Spectrographic analysis of a residue from a heating in a platinum crucible gave strong lines of Pt, K, and Na. Clearly, in all of the anlyses of K_2S above, some part of the sample was missing; two possibilities are that it contained Na or had been contaminated with oxygen.

In melting experiments in evacuated glass containers, Cerac K_2S began melting below 300°C and melted over a long range of at least 200°. Upon melting, the samples separated into two zones. The powder X-ray diffractogram of one zone was that of K_2SO_4; the diffractogram of the other zone was not identified by a search of the ASTM files.[7]

Cerac K_2S was heated under vacuum in Knudsen cells of several materials. The experiments and their results are summarized in Table I. None of the crucibles contained the heated samples satisfactorily. The results of these heating experiments and of the melting experiments above indicated that the Cerac K_2S was impure.

Samples of Cerac K_2S were deliberately exposed to the atmosphere for varying lengths of time. On other occasions, samples were indavertently exposed to the atmosphere. In such cases, subsequent X-ray diffractograms of powders exhibited increased intensity of the "extra lines" mentioned above, and additional unidentified lines. The intensities of the "extra lines" were roughly proportional to the length of atmospheric exposure.

It was concluded that potassium sulfide as supplied by Cerac was not pure and contained some oxide or hydroxide and possibly some KHS and K_2S_x. The presence of impurities explains its low and indistinct melting point. Chemical analyses gave varying results, but were in line with the proposition that the material was impure.

One interpretation of the results of the chemical analyses is that the samples contained both K_2S and Na_2S. For instance, if the sample contained 63.9% K by weight, it could have been $K_2S + 0.15\ Na_2S$. However, other evidence indicated that the samples also contained oxygen.

When the material was heated above its melting point, a reaction equivalent to the following one occurred:

$$4\ K_2O(s) + K_2S(s) = K_2SO_4(s) + 8\ K(g) \qquad (2)$$

The $K_2SO_4(s)$ was found in the residue. In effusion experiments, the K(g) was seen to condense from the effusate, though, as will be seen, evaporation of pure K_2S also produces K(g).

In view of the impurities and low melting point of Cerac K_2S, it was abandoned as unsatisfactory for vaporization studies.

PREPARATION OF K_2S

Pure K_2S was successfully prepared by us by reaction of the elements. Two methods were developed, one a sealed-tube method and the other an open method in a drybox under argon. The latter method was adopted. To facilitate the latter method, a stainless-steel, evacuable drybox which had been in storage at the Lewis Research Center was transported to our laboratory.

The sealed-tube method was executed at the Lewis Research Center. In a drybox a Vycor tube containing two Vycor boats was loaded with a known amount of sulfur in one boat and a stoichiometric excess of potassium in the other boat. The tube was evacuated via a vacuum line leading into the box, the evacuation line was closed, the tube was removed from the box and sealed by a glass blower. The tube was placed in a gradient furnace with the sulfur boat at 400°C and the potassium boat at 150°C. The sulfur distilled onto the potassium, K_2S was produced, and excess potassium remained. The tube was reversed in the furnace, the end containing K_2S was raised to 450°C while the other end was outside the furnace. The excess potassium distilled off, and K_2S was left in the hot end.

The second method of preparing K_2S was patterned after that of Dworkin and Bredig,[3] and was accomplished in our laboratory. Approximately 5 g of highly pure potassium was placed in a nickel crucible in the drybox. The crucible was placed in the bottom of a vertical Pyrex glass tube, as shown in Figure 2. The crucible and lower part of the tube were heated with a heating tape to 180-190°C. Through a glass funnel highly pure sulfur crystals were added slowly to the potassium until ca. 80% of the stoichiometric amount of sulfur had been added.

During this operation it was necessary to keep the upper end of the tube covered because the reaction was so fast and violent that parts of the sulfur were blown away as a fine dust of orange amorphous sulfur. In our first preparation, the inside of the drybox was covered with this dust.

The open end of the tube was closed with a vacuum-tight cap fitted with a vacuum stopcock. The assembly was removed from the drybox, attached to a vacuum line via the stopcock and evacuated. The lower end of the assembly containing the nickel crucible and sample was heated at 450°C until the excess potassium was distilled to the upper part of the tube walls. The stopcock was closed and the evacuated tube was returned to the drybox and opened, and the sample was removed.

The resulting sample was composed of a white fraction and various amounts of material of other colors ranging from yellow through orange. The white fraction was separated manually. X-ray and chemical analyses showed the white fraction to be K_2S. The other fractions probably were polysulfides. With care, a yield of 65-70% K_2S, based on amount of sulfur used, could be obtained. In one preparation, 1.5340 g of sulfur were used and 3.5880 g of K_2S were obtained; the yield was 68%.

In Table II are given the Debye-Scherrer X-ray diffractograms of the white fraction and of the orange fraction from the preparation with a 68% yield of the white fraction.

CRUCIBLE STUDIES WITH PURE K_2S

Most of the results in the earlier search for a suitable crucible material turned out to be not helpful, because the Cerac K_2S was impure, and effects due to interactions between K_2S and the crucible material could not be distinguished from effects due to the presence of impurities, particularly oxygen. With pure K_2S synthesized at LRC and in our laboratory, a search for suitable crucible materials was conducted.

Metallic Crucibles:

One series of experiments tested crucibles of Inconel, nickel, platinum, tungsten, and ordinary graphite from Poco Graphite, Inc. The results on the first four are summarized in Table III. Inconel was tested because it was the material used to contain K_2S for melting-point and heat-capacity measurements by Dworkin and Bredig.[3] Nickel was tested because of its similarity to Inconel. Platinum was tested as an often-inert substance. Tungsten was tested because it has been used successfully as a crucible for sulfides at high temperatures.[8,9] As the table shows, each of the metallic materials proved unsatisfactory.

Graphite Crucibles:

The experiments with Poco graphite crucibles indicated that graphite would be a suitable crucible material. The experiments were done at 850°C, the highest temperature at which at that time we anticipated doing torsion-effusion experiments with K_2S. No mass loss from the crucibles themselves was found. The samples changed color from white to yellow, but their X-ray patterns had the lines of K_2S after each experiment. No evidence of chemical interaction between samples and crucibles was found.

On the strength of the results above, torsion-effusion experiments with K_2S in cells of Poco graphite were conducted; their results are presented in a subsequent section. From these experiments we learned that K_2S vapor was lost from the graphite crucibles by diffusion through the bulk. Because of this inadequacy of ordinary graphite, the search for a crucible material was continued.

In another set of experiments, K_2S was heated in crucibles of Inconel, rhenium, and alumina.

Inconel Crucible, Further Studies:

Even though earlier experiments had shown Inconel to be an unsuitable crucible material, experiments with it were repeated. The reason for the new trials was a telephone conversation with one of the authors (Dworkin) of the paper which reported the melting point of K_2S measured in an Inconel container.[3] He was definite on the fact that they had observed no reaction between K_2S and the container.

Two heatings of a sample initially 207 mg of K_2S in an inconel crucible were done, the first at 780°C for 1 hr., the second at 876°C for 2 hrs. The first gave 22 mg mass loss and the second 38 mg. After the first heating, the X-ray diffractogram of the residue was that of K_2S with 6 additional lines, the most intense being 1/5 as intense as the most intense line of K_2S. After the second heating, the X-ray diffractogram of the sample had no lines of K_2S; 5 of the 6 unidentified lines seen after the first heating were the most intense among 23 lines measured. The X-ray diffractogram of the residue could not be identified by searching the ASTM files. The cell was washed, outgassed, and weighed; it weighed 35 mg less than it did before the heating experiments.

These experiments confirm that Inconel is unsuitable as a crucible material for vaporization studies of K_2S. The observation of Dworkin and Bredig[3] that Inconel did not react with K_2S must be related to the fact that their Inconel capsule was sealed so that no vapor could escape. Perhaps passification or equilibration with the Inconel surface prevented extensive reaction in the closed system.

Rhenium Crucible:

A rhenium crucible was tested in our laboratory by experiments similar to those used for crucibles of other materials and was tested at the Lewis Research Center in a longer-term, mass-spectrometric study of K_2S. The same crucible was used in both tests.

The experiments with rhenium in our laboratory differed in one important way from previous crucible tests, viz., after each heating the sample was removed and the empty crucible was weighed. Four successive heatings were done with a sample initially 200 mg of K_2S: 800°C for 1 hr; 850°C for 1 hr; 875°C for 1 hr; and 950°C for 1 hr. Total mass-losses were 2 mg, 22 mg, 23 mg, and 28 mg, respectively. Mass change of the empty crucible was minor throughout. After the second and last heatings, the crucible was washed, outgassed, and weighed. After the second heating the crucible mass was the same as that at the start, 18.812 g; after the fourth heating it had lost 2 mg. The X-ray diffractograms of the sample contained the lines of K_2S after each heating.

The results above indicated that rhenium would be a suitable crucible material. However, a mass-spectrometric study of the vaporization of K_2S done at the Lewis Research Center with a rhenium crucible demonstrated the opposite. The experiment involved heating the sample over much longer periods of time than those in our experiments and produced extensive reaction between K_2S and rhenium which finally ruined the sample.

Crucibles constructed of three chemical compounds and of high-density graphite were tested as containers for vaporization of K_2S. The compounds were titanium boride, zirconium oxide, and aluminum oxide.

Titanium Boride Crucible:

Fifty-six milligrams of K_2S was heated in vacuum in a titanium boride crucible with a loosely fitting lid without an orifice, with a body weight of 1.3509 g and a lid weight of 0.2526 g. The heating conditions were 700°C for 14 hours. The body lost 22 mg (in addition to the sample loss) and the lid lost 5 mg. Five horizontal circular cracks around the circumference of the body were caused. Discoloration around the cracks on the outside of the crucible indicated that sample had flowed through the cracks. The conclusion from the observations was that titanium boride is not suitable as a crucible material for K_2S.

Zirconia Crucibles:

Eighty-four mg of K_2S was heated in a zirconium oxide crucible with a loosely fitting lid containing a small orifice; the weights of the crucible body and lid were 2.2157 g and 0.3145 g, respectively. The heatings were at 780°C for 12 hours and at 910° for 13 hours.

During the first heating, 9 mg was lost. The sample was sintered or melted and adhered to the bottom of the crucible. Portions were removed for X-ray analysis and for chemical analysis by titration with standard acid. The latter gave a formula of K_xS with $x - 1.70 \pm 0.15$. Results from the X-ray diffractometry are given in a subsequent section of this report. During the second heating 70 mg of mass was lost, 68 mg from the body and sample, and 2 mg from the lid. No sample was left in the crucible. The crucible was washed with water and the washings were titrated with standard acid; the resulting alkalinity was equivalent to 0.4 mg of K_2S.

The mass of the zirconia crucible, after washing and oven drying, was: body, 2.2204 g; lid, 0.3150 g. The 5 mg gain in the body could have been due to the fact that the crucible was oven dried and not outgassed at high temperature in vacuum before final weighing. The indication was that 5 mg of the sample was somehow taken up in the bulk of the crucible.

Alumina Crucibles:

Samples of K_2S were heated in two alumina crucibles without orifices, but with loose-fitting lids. The heatings in one crucible will be referred to as Series A and those in the other crucible will be referred to as Series B. Series A involved a sample with initial weight of 200 mg and four sequential heatings in the induction furnace with the alumina cell inside of a graphite susceptor. Series B involved a sample with initial weight of 190 mg and three sequential heatings in another alumina cell in a graphite susceptor. The lid and body of the crucible in Series B were ground so that the lid might seal the crucible better, though it simply lay loosely atop the body.

The first heating in Series A was at 850°C for 1 hours. Mass loss was 18 mg. Afterwards the sample was yellow and sintered to the bottom of the crucible. A small amount of the sample was removed for X-ray analysis and found to contain lines of K_2S, the five strongest lines of α-Al_2O_3, and other lines which were not identified.

The second heating in Series A was a continuation of the heating of the same sample, but at 875°C for 1 hr. Mass loss was 31 mg. The sample became a darker yellow or brown in color and was still sintered to the bottom of the crucible. X-ray analysis showed lines of K_2S along with the unidentified lines found in the first heating, but the latter with higher intensitities. Alumina lines were no longer present.

The third heating in Series A was additional heating of the same sample, but at 930° for 1 hr. Mass loss was 60 mg. The condition of the sample was as before except the color was brown. X-ray lines of K_2S were still found along with the unidentified lines; the intensities of the latter had increased to approximately those of K_2S. The results of the X-ray diffractometry are given subsequently in this report.

The fourth heating in Series A was a continuation from the third heating, at 930°C for 2 hr. The rest of the sample was lost and the mass of the crucible was the same, within 1 mg, as that before the sample was loaded for this series. To establish that the sample was gone, the crucible was heated further at 1300°C for 1 hr. The latter heating caused an increase in the crucible mass of 2 ± 1 mg.

The first heating in Series B was at 760°C for one hour. Mass loss was 24 mg. The residue was yellow. Two small amounts of the residue were removed, one for X-ray analysis and one for titration.

X-ray analysis gave the lines of K_2S and the same unidentified lines as observed in Series A. No lines of alumina were present. The result of titration of the residue was used to calculate a subscript for K in K_xS, and $x = 1.853 \pm .006$ was obtained; the uncertainty is the standard deviation among titrations of three aliquots of the same residue sample.

The second heating in Series B was a continuation of the first, but at 850°C for one hour. Mass loss was 56 mg. The residue was dark yellow. X-ray analysis showed K_2S in the residue and the same unidentified lines with relative intensities greater than after the first heating.

The third heating in Series B was a continuation of the second, but at 930°C for 1 hour. The balance of the sample, 96 mg, was lost in this heating. The crucible was washed with distilled water and the washings were titrated; alkalinity equivalent to 0.56 ± 0.01 mg of K_2S was found. The washed crucible was dried and outgassed in vacuum at 1300°C for 1 hour; the crucible then was weighed and was found to have gained 3 ± 1 mg since the beginning of Series B.

High-Density Graphite Crucibles:

In an attempt to deal with the problem of bulk diffusion of K_2S out of graphite crucibles, heating experiments were done with crucibles of high-density graphite obtained from Ultra-Carbon Corp. The graphite previously used was pyrolytic graphite with a density of 1.51 ± 0.01 g/cc. The high-density graphite had a density of 1.81 ± 0.01 g/cc. Theoretical density of graphite is 2.26 g/cc. The experiments were in an inductively heated furnace surrounded by a glass vacuum envelope.

Two types of heating experiments were done with crucibles of high-density graphite: closed-crucible experiments and orifice-effusion experiments. Closed crucible experiments were with a crucible with a tightly fitting lid without an orifice. Orifice-effusion experiments were with a crucible of the same design, but with an orifice in the lid.

One hundred and thirteen milligrams of K_2S was heated in a closed crucible with a body weight of 2.662 g and lid weight of 0.426 g. The heating was in the induction furnace, with a molybdenum radiation shield, at 750°C for 6.5 hrs. No deposit was visible on the glass envelope.

The total weight of the crucible and sample after the heating was 3.200 g, thus no more than 1 mg was lost during the heating. The sample was melted or sintered to the bottom of the crucible. No alkalinity was found in washings from the glass envelope around the furnace during the heating.

Heating was continued with the same cell and sample at 820°C for 4 hours. No deposit was visible on the glass envelope. The mass of crucible and sample after heating was still 3.200 g.

Heating was continued at 830°C for another 7 hours. No deposit was visible on the glass envelope; washings from the same gave no alkalinity by titration. The mass of the crucible and sample after heating was 3.199 g. A small quantity

(3 mg) of the sample was removed for an X-ray diffractogram. The residue was still fused or sintered to the bottom of the crucible.

Heating was continued at 930°C for 6 hrs. No deposit was visible on the glass envelope; titration of washings from the envelope gave alkalinity equivalent to 0.7 mg of potassium. The mass of the crucible and sample after heating was 3.190 g; with consideration of the 3 mg removed before for X-ray analysis, this weight shows that 6 mg was lost during heating. A small amount of residue was removed for X-ray diffractometry.

The crucible and lid from the heatings above were washed and dried and weighed. Crucible weight was 2.655 g and lid weight was 0.427 g. After out-gassing at 1300°C in vacuum, the crucible weight was 2.650 g and the lid weight was 0.428 g. The crucible had lost 12 mg and the lid had gained 2 mg. From the washings from the crucible and lid, 9.5 mg of the graphite was recovered. The washings from the crucible and lid were titrated with standard acid, and alkalinity equivalent to 39.6 mg of potassium, or 55.8 mg of K_2S, was found.

No significant weight loss was found in the heating experiments with K_2S in a closed, high-density-graphite crucible. However, titration of the washings from the crucible located only 55.8 mg of the 113 mg of K_2S which should have been present.

Experiments with high-density graphite crucibles were continued. Ninety-seven milligrams of K_2S was heated in the induction furnace in a crucible with a body weight of 2.648 g and a lid weight of 1.910 g and with cylindrical orifice with area of 4.26 cm^2 and with transmission probability of 0.250.

The first heating was at 810°C for 28 hrs. No depsoit was visible on the glass envelope. The weight of the crucible body and sample was 2.735 g and of the lid was 1.907 g, a decrease in total weight of 13 mg. The sample was melted or sintered to the bottom of the crucible. Titration of washings from the glass envelope gave no alkalinity. Eight mg of the residue was removed for X-ray diffractometry and titration. The latter gave a formula of K_xS with $x = 1.80 \pm 0.10$; originally the sample had a formula with $x = 1.90 \pm 0.10$.

The second heating was at 910°C for 13 hrs. The weight loss was 23 mg. No deposit was visible on the glass envelope, but titration of the washings from the envelope gave alkalinity equivalent to 5 mg of potassium. Appearance of the residue was still molten or sintered. Four milligrams was removed for X-ray diffractometry and titration. The latter gave a formula of K_xS with $x = 1.40 \pm 0.07$.

At the start of this heating, the sample was 76 mg of $K_{1.80}S$ and at the finish it was 53 mg of $K_{1.40}S$. The former contains 20 mg more potassium than does the latter. The weight loss was 23 mg. Thus, this change agreed reasonably with the idea that only potassium was being lost from the sample.

The third heating was again at 910° for 13 hrs. The weight loss was 15 mg. Seven milligrams, which contained 4 mg of graphite, were removed for analysis by titration. The result was K_xS with $x = 0.67 \pm 0.10$.

At the start of the third heating, the sample was 49 mg of $K_{1.40}S$ and at the finish it was 33 mg of $K_{0.67}S$. The former contained 16 mg more potassium that did the latter. The weight loss was 16 mg. Thus, this change agreed with the idea that only potassium was being lost from the sample.

The fourth heating was at 1010°C for 12 hrs. The weight loss was 12 mg. The residue was yellow, hard, and sintered to the bottom of the crucible so that it was very hard to remove. The entire residue was dissolved by washing the crucible with water. The washings were titrated with standard acid. Simple accounting gives the mass of the residue as 30 mg. On the basis of a 30-mg sample of K_xS, the titration gave $x = 1.07$; however, the last number is highly uncertain, because the accounting which yielded a residue mass of 30 mg included no changes in the crucible mass.

After washing and drying the crucible, its mass was 2.625 mg. Thus, the crucible lost 23 mg during the four heatings and other treatments. Four milligrams were known to have been scraped out after the third heating. Experience with the heatings in a closed cell showed that ca. 10 mg of graphite was taken up physically in the melted sample. Thus, a net weight loss in the crucible of ca. 9 mg is indicated.

If the crucible lost 9 mg, then the final sample mass was 39 mg, and the formula of the sample residue was K_xS with $x = 0.63$, again with considerable uncertainty. It is worth noting that the last number is in good agreement with the number, $x = 0.67 \pm 0.10$, found for the residue after the third heating. Thus, the latter number may give the stoichiometry of the congruently vaporizing or azeotropic composition in the K-S system. The formula is near K_2S_3. In descriptions of vapor-pressure measurements later in this report, this general stoichimetry will be seen to be favored.

We concluded from the heating experiments with zirconia, alumina, and high-density graphite crucibles that any of these materials would be suitable for containin K_2S in vaporization experiments. Vapor-pressure measurements in crucibles of high-density graphite and of alumina are described subsequently in this report.

X-RAY DIFFRACTOGRAMS

A revealing general picture arose from examination of X-ray diffractograms of K_2S residues which had been heated in zirconia, high-density graphite, and alumina. Initially, before a large fraction of the sample had vaporized, the diffractograms contained lines due to K_2S along with additional lines which grew in as the sample vaporized. Most significant was the fact that the additional lines were very nearly the same, regardless of which type of crucible was being used.

To identify the additional lines, the X-ray diffractogram of K_2S_2 was calculated from its lattice parameters given in the literature.[10] In Table IV, the calculated lines of K_2S_2 are compared with the additional (wrt K_2S) lines from residues heated in alumina, high-density graphite, and zirconia. Intensities of K_2S_2 lines are experimental results from the reference paper.[10]

The very high correlation between the X-ray diffractogram of K_2S_2 and the additional lines in the table above means that the new phase that grows in while K_2S is vaporized is K_2S_2. The fact that the residues in vaporization experiments became progressively sulfur rich indicates that potassium is vaporized. Mass spectrometry at Lewis Research Center has shown that the vapor over K_2S is approximately 99% potassium early in the vaporization.

The results can be interpreted best by considering that the vaporization reaction of $K_2S(s)$ is incongruent and produces predominantly potassium in the vapor and a condensed phase which, when cooled, produces solid K_2S_2. At temperatures where the vaporization was studied, K_2S_2 is a liquid. If K_2S_2 melts congruently and remains stable, then the vaporization reaction of $K_2S(s)$ might be

$$2K_2S(s) = K_2S_2(l) + 2K(g) \qquad (3)$$

The melting point of K_2S_2 is 471°C, and other potassium polysulfides have even lower melting points. The incongruent vaporization by reaction (3) explains why samples seemed to be melted or sintered even in the vaporization experiments at the lowest temperatures.

As vaporization of K_2S from a Knudsen cell proceeds, the composition of the condensed phase eventually reaches that of K_2S_2, then K_2S_3, etc., until a congruently vaporizing or azeotropic composition is reached. The sample would vaporize with this composition until all was exhausted. The experiments in high-density graphite indicated that the azeotropic composition might be near that of K_2S_3.

MEASUREMENT OF THE VAPOR PRESSURE OF K_2S

Full-scale experiments with our Knudsen-torsion-effusion equipment were done with K_2S in high-density graphite and alumina crucibles. Two experiments were done with high-density, graphite crucibles. The first was done with a crucible machined from high-density graphite rod from Ultra-Carbon Corp. The second was done with a crucible made by Ultra-Carbon from their high-density graphite and subsequently treated by them to increase the density of all surfaces of the crucible.

One experiment was done with K_2S in an alumina crucible. The torsion-effusion cell of alumina was of an unusual design. Personnel at the Lewis Research Center provided us with two, small, cylindrical, alumina crucibles, each with a tight-fitting lid and with an orifice in the side. A graphite holder was constructed to hold the crucibles in the positions shown in Figure 3, so that the assembly functioned as a torsion-effusion cell.

High-Density Graphite, Experiment 1.

The first torsion-effusion experiment in high-density graphite and its results were reported in the literature.[11] They are summarized here.

The initial mass of K_2S in the vapor-pressure experiments was 400 ± 1 mg (200 ± 1 mg in each of the two chambers of the effusion cell). Early in the experiment, until 70 mg of sample had been lost, the vapor pressures measured by torsion effusion were in good agreement with those measured by Knudsen effusion. After 70 mg had been lost, the Knudsen-effusion pressures became more than twice as great as those obtained by torsion effusion. The onset of this effect was sudden, over a period during which no more than 1 mg of sample was lost. The P vs T relationship from the torsion-effusion measurements was unaffected by this change.

The increase in Knudsen pressures was attributed to the onset of bulk diffusion of potassium through the walls of the graphite cell. No effect on torsion pressures was imparted because the diffusion and subsequent vaporization of the potassium was uniform in direction and symmetrical on both ends of the effusion cell. Thus, the Knudsen-effusion results were not used in the thermodynamic analyses and all results reported here are based on the torsion-effusion results.

Vapor pressures were measured at 53 temperatures ranging from 1080 to 1171 K. When the first measurement was made, 395 mg of the original 400 mg of sample remained; when the last measurement was made, 35 mg of sample remained. The results could be divided into two groups, one including the first 35 measurements during which 205 mg of sample vaporized, and the other including the last 18 measurements during which 155 mg vaporized. Each group exhibited distinct linear dependence of log P on 1/T. The data are plotted in Figure 4. For the first group:

$$\log(P/Pa) - -(15200 \pm 500)K/T + 13.85 \pm 0.42 \tag{4}$$

For the second group:

$$\log(P/Pa) = -(15000 \pm 700)K/T + 13.50 \pm 0.60 \tag{5}$$

Division of the data into two groups was taken to mean that the vaporization reaction for the first group was different from that for the second group. The composition of the sample at the time of the change into the second group was calculated on the assumption that the mass loss, 210 mg, was due entirely to loss of K(g), in line with the mass spectrometric results. With an estimated uncertainty, the result was $K_{2.0\pm0.1}S_4$. The log P vs 1/T relationship of the second group was obeyed until less than 35 mg of sample remained, after which time the measured vapor pressure dropped rapidly with further loss of mass at a given temperature. The latter effect was taken to represent undersaturation in the cell due to the small surface area of the remaining sample.

The vaporization reaction for the first group of data was taken to be:

$$2/3\ K_2S(s) \rightarrow 1/6\ K_2S_4(l) + K(g) \tag{6}$$

The product K_2S_4 is written as a liquid in these experiments, because its melting point is 159°C[4]. The K_2S_4 composition was taken to be congruently vaporizing or azeotropic with negligible dependence on temperature in the range of the present experiments. Then the vaporization reaction for the second group of data was:

$$1/4\ K_2S_4(l) \rightarrow 1/2\ K(g) + 1/2\ S_2(g) \tag{7}$$

Free energy functions, Φ, of $K_2S_4(l)$ were estimated by the following relationships:

$$\Phi[K_2S_4(s)] = \Phi[K_2S(s)] + 3(\Phi[Na_2O_2(s)] - \Phi[Na_2O(s)]) \tag{8}$$

$$\Phi[K_2S_4(l)] = \Phi[K_2S_4(s)] + 2(\Phi[Na_2S(l)] - \Phi[Na_2S(s)]) \tag{9}$$

Values of free energy functions required in equations (8) and (9) were obtained from the JANAF Tables.[12] Free energy functions of K(g) and $S_2(g)$ also were obtained from the JANAF Tables. Table V gives free energy functions used in this work.

Equilibrium constants for reactions (6) and (7) were calculated from:

$$K_{eq}[\text{reaction (6)}] = P \tag{10}$$

$$K_{eq}[\text{reaction (7)}] = P_K^{1/2} = 0.4386P \tag{11}$$

Third-law analysis with these equilibrium constants and the free energy functions from Table V gave the following enthalpy increments of reactions (6) and (7):

$$\Delta H°(298\ K)[\text{reaction(6)}] = 223.4 \pm 0.4\ kJ/mol$$

$$\Delta H°(298\ K)[\text{reaction(7)}] = 271.5 \pm 0.2\ kJ/mol$$

in which the uncertainties are standard deviations of the mean. These results, when combined with $\Delta H°(298\ K)$ of K(g)[12], 89.16 kJ/mol, and of $S_2(g)$[12], 128.5 kJ/mol, give $\Delta H°(298\ K)$ of $K_2S(s)$, -364 ± 12 kJ/mol, in which the uncertainty is estimated.

The latter value agrees with the value of Rengade and Costeanu[13] -365.2 kJ/mol but not with others,[11] which range from -376 to -406 kJ/mol.

High-Density Graphite, Experiment 2.

In the second experiment in the Knudsen-torsion-effusion apparatus with K_2S in high-density graphite, the graphite crucible had been treated at Ultra-Carbon Corporation to densify the surfaces, but otherwise the procedures were the same as in previous experiments. A blank experiment with the cell empty gave zero vapor pressure by both Knudsen and torsion. In the vapor-pressure experiment, the amount of sample was 395.2 mg and the temperature range was 760-860°C.

The course of the second experiment was approximately that of the first but much less consistency was found. While the first 70 mg of sample were being lost, the ratio of Knudsen and torsion vapor pressures, P_K/P_T, was in the range 0.66-0.76. While the total mass loss changed from 70 mg to 190 mg , P_K/P_T was within the range 4.0-12.0. Then, while the remainder of the sample was being lost, P_K/P_T was within 15-30. The appearance was that up to a mass loss of 70 mg vapor was lost only through the orifice, and Knudsen and torsion pressures agreed roughly. Then diffusion of the sample through the cell wall caused the apparent Knudsen pressures to be too high.

A plot of the logarithms of the torsion pressures vs K/T is given in Figure 5. Data in four groups are identified by four types of symbols. The circles represent data taken before 70 mg of sample had been lost while Knudsen and torsion pressures were in fair agreement. The closed circle represents the last vapor pressure measurement in this group. Squares represent data in the group taken in the mass-loss range 70-190 mg. The closed square represents the first measurement and the ticked square represents the last measurement in this mass range. The next group of measurements were in the mass-loss range 190-280 mg and are represented in Figure 5 by triangles. The ticked triangle represents the first and the closed triangle represents the last measurement in this group. The last group of measurements were in the range 280-395 mg and exhausted the sample from the cell. They are represented by diamonds in Figure 5 and the first is represented by the closed diamond. The ticked diamond represents the last measurement.

The first two groups of torsion pressures correspond to the regions when the P_K/P_T ratios were 0.66-0.76 and 4.0-12.0, respectively. The implication is that, when sample diffused through the walls and vaporized from the outside of the crucible, the vaporization was not symmetric and decreased the torsion pressure. The second break between groups was similarly correlated with an abrupt change in the P_K/P_T ratio. No such correlation existed with the third break. With the assumption that only K(g) is lost from the sample, the composition at the second break was calculated from the mass loss to be $K_2S_{3.3\pm0.4}$.

The third break occurred after a mass loss greater than the mass of potassium in the sample had been lost. It follows that at some time before this break the sample had begun losing sulfur by vaporization. This observation calls into question the assumption that only potassium is lost from the sample at any time. However, mass spectrometry at Lewis Research Center showed that only K(g) is lost initially. The assumption is probably good up to the condensed-phase composition corresponding to K_2S_4.

In spite of the apparent inconsistencies between the results of these experiments and the earlier ones in a high-density graphite crucible, several similarities exist. In both experiments, the Knudsen and torsion pressures agreed reasonably well until high Knudsen pressures indicated sample was diffusing through the walls. The second break in the log P-vs-1/T plot of data from the second experiment occurred when the sample composition based on the assumption that K(g) only was vaporized was $K_2S_{3.3\pm0.4}$; in the first experiment one break only was observed, but at a sample composition of $K_2S_{4\pm0.2}$, a composition close enough that the two breaks might be related.

K$_2$S Vapor Pressure in Alumina Crucibles.

Except for the difference in crucible design, the vapor-pressure experiment with K_2S in alumina was done by the same procedure used in the experiments with high-density graphite crucibles. The effusion-cell, composed of two alumina crucibles as described earlier, was loaded with 323.5 mg of K_2S, equally divided between the two cells.

Until 16 mg of sample had been lost the Knudsen and torsion pressures agreed well with P_K/P_T in the range 1.0-1.2. After 16 mg had been lost, P_K/P_T was in the range 4.0-15.0 until the experiment was terminated.

The torsion results are plotted as log P vs 1/T in Figure 6. The vapor pressures fell into four regions represented by circles for the first (in time) region, squares for the second region, triangles for the third region, and diamonds for the fourth region.

The vapor pressures represented by circles in Figure 6 were measured while the first 16 mg of sample was being lost. At the time that P_K/P_T increased into the 4.0-15.0 range, the torsion pressures increased sharply. The filled circle represents the last vapor pressure measured before the increase and the filled square the first measured thereafter. The last vapor pressure measured in the second region is represented by the ticked square and the first in the third region by the ticked triangle; clearly the vapor pressures decreased in the third region and were roughly equal to those in the first region. In the fourth region, the vapor pressures increased initially to the level of those in the second region, then they fell away precipitously by a factor of several hundred. The closed triangle represents the last measurement in the third region, the closed diamond the first in the fourth region, and the ticked diamond the last measurement.

At the end of the experiment, sample remained in each alumina crucible. The apparatus was vented with dry argon. The pendulum was disassembled while argon flowed upward in the apparatus. The crucibles were removed quickly, placed in a desiccator, and transferred to the dry box. Total time of exposure of the crucibles to the atmosphere was less than one minute. Some sample residue was removed from each crucible and stored for X-ray diffraction analysis. Some sample residue was removed from each crucible, weighed, and titrated with standard acid. With the assumption that the sample was K and S only, the weighings and titrations gave the following compositions: Left crucible, $K_2S_{1.6\pm0.3}$; right crucible, $K_2S_{1.2\pm0.2}$. The Debye-Scherrer X-ray diffractograms of the samples are given in Table VI and are discussed subsequently.

The break from the first region to the second in Figure 6 was associated with the change in P_K/P_T from the range 1.0-1.5 to the range 4.0-15.0. Neither of the other two breaks could be correlated with any changes in P_K/P_T. The first break and the increase in P_K/P_T were due to the sample diffusing through the crucible wall and vaporizing from the outside of the wall. At this point, P_K increased greatly, but the effect on P_T was less because vaporization in several directions had a cancelling effect on the torque. However, the cancelling was not complete and the increase of P_T in the second region occurred.

At the time of the break from the second region to the third region in Figure 6, the sample composition calculated from the total mass loss and the assumption that only K(g) was lost was $K_2S_{3.14\pm0.10}$. This break might be related to breaks seen in experiments in high-density graphite crucibles at compositions from K_2S_3 - K_2S_4 calculated on the same basis. The chemical analyses and the X-ray diffractograms (discussed subsequently) of the residues contradict these formulas of the samples, but not the possibility that the breaks may be related.

The initial increase in vapor pressure after the break from the third region to the fourth region in Figure 6 indicates that sample diffusing through the walls of the crucible was not doing so uniformly. In the third region, a vaporization process occurring in both crucibles produced vapor which ultimately vaporized off of the two crucibles in directions which caused cancellation of part of the torque. At the break, the process changed in one crucible, but not the other, and its cancelling effect was lost. Thus, the torque and the apparent torsion pressure increased. After four pressures in the fourth region were measured, the process changed in the second crucible and the torque dropped by a factor of several hundred.

The final break, after four measurements in the fourth region, down to very low torque and the presence of sample in the crucibles at the end are phenomena unique to the experiment in alumina crucibles. Apparently, a chemical change in the sample upon loss of potassium occurred at a composition within $K_2S_{2.0\pm0.6}$ and caused a vapor pressure drop of several hundred. Nothing approaching such a drastic change in vapor pressure with composition has been observed in other experiments with K_2S, except at the point of total exhaustion of the sample.

Another explanation of the sharp drop in vapor pressure in the fourth region in Figure 6, would be a fortuitous perfect cancellation of torque from the two crucibles due to opposite angular direction of evaporating sample. The probability of such an effect is small, but no probable chemical penomenon which explains the observation is apparent.

The formulas of the sample residues at the end of the experiment, both within $K_2S_{2.0\pm0.6}$, and the overall formula at the break between the second and third regions, $K_2S_{3.14\pm0.10}$, should be compared; they contradict the notion that potassium is lost by vaporization from K_2S at a rate greater than that at which sulfur is lost. The compositions at the end contain relatively less sulfur than that at the break. Two possible resolutions of this contradiction follow:

(1) Possibly both potassium and sulfur were vaporizing while measurements in the first and second regions were being made. Then assigning all of the weight loss to potassium would imply a composition too rich in sulfur. (2) Some unknown reaction of the sample with the alumina crucible might have caused potassium to have been retained in preference to sulfur. The former possibility is the more likely. No evidence of the latter was found.

Despite the variety of results obtained in the vapor pressure experiments with K_2S, some consistencies exist and should not be overlooked. In both torsion-effusion experiments in high-density graphite and in the experiment in alumina, the initial measurements before the first break, before loss of mass by diffusion through the bulk of the cell, were in acceptable agreement. With the assumption that initial vaporization of each sample was by reaction (8), the third-law $\Delta H°(298\ K)$ was for the first experiment in high-density graphite, 223.4±0.4 kJ/mol, for the second experiment in high-density graphite, 222.4±0.7 kJ/mol, and for the experiment in alumina, 231.0±0.5 kJ/mol. The uncertainties are standard deviations of the means, and reflect none of the possible systematic errors in high-temperature vaporization experiments. The three results are in reasonably good agreement. The slightly higher value from the experiment in alumina yields $\Delta H°(298\ K)$ of $K_2S(s)$ of -376±12 kJ/mol when combined with results from the first measurement in high-density graphite. That result agrees with the one from JANAF,[12] 377±13 kJ/mol. Equations (4) and (5), which are the same within experimental error, give the vapor pressure accurately within this region.

Another consistency was that in each of the three experiments a break in the log P vs 1/T plots occurred when the sample composition (calculated from the assumption that only K vaporized) was in the range K_2S_3 - K_2S_4. The indication is that a change in the vaporization reaction occurs in this range. Even though chemical analysis and X-ray diffraction results from the experiment in alumina contradict the chemical formula, it is a useful index of the point of the transition, if the assumptions underlying it are kept in mind.

VAPORIZATION OF K_2SO_3 AND $K_2S_2O_5$

Our initial studies of the high-temperature behavior of K_2SO_3(s) were done with K_2SO_3 obtained from commercial sources, viz., Fisher Scientific Co. and Baker Analyzed Reagent from Matheson, Coleman, and Bell. Labels on the bottles gave an impurity total less than 0.5%. Samples were dried at 110°C and stored in a desiccator over $CaSO_4$.

A matter worth clarifying here is the fact that K_2SO_3 apparently has no hydrate. This mention is necessary because the ASTM Index[7] of X-ray diffraction patterns gives a pattern for $K_2SO_3 \cdot 2H_2O$, but none for K_2SO_3. All starting materials in our work had the X-ray diffraction pattern of "$K_2SO_3 \cdot 2H_2O$" but gave no evidence of being hydrated. Probably the material on which the ASTM pattern was based was mistakenly identified as a hydrate. Old work from the eighteenth century reports the existence of a dihydrate;[5] perhaps this is the source of a concept of a dihydrate.

Chemical analyses at LRC for potassium in Fisher K_2SO_3 gave 50.0% and in Baker K_2SO_3 gave 50.2%, both being in line with the calculated value for K_2SO_3 of 49.4%. The dihydrate would have 40.2% potassium.

Our first vacuum heating experiments with K_2SO_3 involved placing the sample in a crucible of boron nitride, machinable glass, porcelain, or platinum and heating in the range 700-800°C in glass vacuum systems. Effusates condensed on the wall of the vacuum systems were observed, the residue in the crucible was studied by X-ray powder diffraction, and the effect on the crucible was noted. The results of these studies were reported in a semiannual report.[14]

To learn the composition of the vapor over K_2SO_3, mass spectrometry of the vapor from K_2SO_3 in a Pt crucible was done at the Lewis Research Center in collaboration with Carl Stearns and Fred Kohl. Two separate experiments were done with two different samples. The first was with a sample of dried Fisher K_2SO_3.

The second was a sample of $K_2S_2O_5$ prepared by reaction of a saturated water solution of K_2SO_3 with SO_2 bubbled through it. In the latter case, decomposition of the $K_2S_2O_5$ at low temperatures in the mass spectrometer produced K_2SO_3.

Initial observations on the K_2SO_3 sample indicated that potassium was the primary effusing species at ca. 700°C. Relative intensities of the shutterable mass spectrometric peaks were $CO_2^+ = 27$, $K^+ = 3600$, and SO_2^+(or S_2^+) = 4.

Essentially the same observations were seen with the $K_2S_2O_5$ starting sample after it had decomposed to K_2SO_3. As the temperature was increased and the degree of decomposition of the sample increased, the K^+ and CO_2^+ intensities decreased and the SO_2^+ intensity increased, but the K^+ intensity was always much greater than that of SO_2^+.

The observations were explained by personnel at Lewis Research Center by postulating that the starting sample contained K_2CO_3. At low temperature the following reaction would occur:

$$K_2CO_3(s) = K_2O(s) + CO_2(g) \tag{12}$$

Then, at high temperature, further reaction would produce K(g) by

$$K_2O(s) + K_2SO_3(s) = K_2SO_4(s) + 2\ K(g). \tag{13}$$

This hypothesis would be in line with observation of small amounts of CO_2 at the high temperatures where the sample was initially studied, observation of K(g) condensing from the effusate, observation of principally K^+ in the mass spectrum, and observation of X-ray diffraction lines of K_2SO_4 in the residue.

Carl Stearns at LRC developed a technique for purifying commerical K_2SO_3 by adding SO_2 to a saturated solution of K_2SO_3 to precipitate $K_2S_2O_5$. The solid $K_2S_2O_5$ was filtered out, washed with SO_2-saturated water, then dried. The K_2SO_3 could be recovered by decomposing the $K_2S_2O_5$ in vacuum at ca. 200°C. The method was applied both at LRC and in our laboratory. It was necessary to control the temperature of the reaction at or below room temperature and to protect the product $K_2S_2O_5$, particularly when the latter was wet. Otherwise the S^{IV} was oxidized to S^{VI} and K_2SO_4 was found in the final product.

Most of the problem of obtaining pure samples of K_2SO_3 were solved by the discovery by J. E. Bennett of Arkansas State University that commerical $K_2S_2O_5$ purchased from Fisher Scientific Co. is pure. Our work, too, indicated that Fisher $K_2S_2O_5$ can be decomposed successfully to K_2SO_3 and SO_2.

Further searches for a suitable crucible material to contain K_2SO_3 were done with pure K_2SO_3 prepared by decomposition of $K_2S_2O_5$. K_2SO_3 was heated in crucibles of four materials: alumina, platinum, graphite, and boron nitride. In one experiment in alumina, a piece of gold wire was added to the sample to test the reaction with gold. The results of these experiments are given in a semiannual report.[15] Our conclusion from these and previous vacuum heating experiments with K_2SO_3 are that platinum and alumina are suitable materials for containing K_2SO_3 in such experiments. The other materials were unsuitable. However, graphite was a suitable container for decomposing $K_2S_2O_5$ to K_2SO_3 and SO_2 at temperatures below 400°C.

Quantitative vaporization experiments were done with $K_2S_2O_5$ in the Knudsen-torsion-effusion apparatus in graphite crucibles and in a very limited experiment the Nuclide mass spectrometer in a graphite crucible. Such experiments with K_2SO_3 were done in the torsion-effusion apparatus in a platinum crucible and in the Nuclide mass spectrometer in an alumina crucible in a molybdenum holder. For a separate purpose, K_2SO_3 was studied in the Nuclide mass spectrometer in a graphite crucible, despite the fact that K_2SO_3 was shown earlier to react with graphite. This latter experiment is reported in a separate section at the end.

Vaporization of $K_2S_2O_5(s)$.

The vaporization reaction of $K_2S_2O_5$ was assumed to be

$$K_2S_2O_5(s) = K_2SO_3(s) + SO_2(g) \tag{14}$$

That $SO_2(g)$ was produced by decomposition of $K_2S_2O_5$ was confirmed in the limited mass-spectrometric experiment with $K_2S_2O_5(s)$. In that experiment, the intensities of the mass spectrometric peaks at m/e values of 64, 65, and 66 were measured at a sample temperature of 148° and of the peaks at m/e values of 64 and 48 at a sample temperature of 184°C and ionizing voltage of 70 ev. The results of the former experiment are presented here as a table in which the first column shows the m/e values, the second column the relative intensities with the total of all three equal to unity, and the third column the expected relative intensities for SO_2^+ calculated from natural abundances of the elements.

m/e	Observed Relative Abundance	Calculated Natural Abundance
64	0.944	0.946
65	0.0091	0.0083
66	0.048	0.046

These results establish that the only important contributor to these peaks was SO_2^+.

The ratio of the intensities of the peaks at m/e = 48 and m/e = 64 was $I_{48}/I_{64} = 0.73$. In this experiment, the only ion with m/e = 48 was SO^+, a fragment of SO_2^+. Thus, an expected ratio of $I_{SO^+}/I_{SO_2^+}$ was established for use in experiments with $K_2SO_3(s)$ at higher temperatures where S_2^+ might contribute at m/e = 64, but not at m/e = 48.

Three studies of the vaporization of $K_2S_2O_5$ were done in the torsion-effusion apparatus. The measured vapor pressures as functions of temperature were fitted by the least-squares method to the equation

$$\log (P/Pa) = -A/T + B \tag{15}$$

In Table VII values of A and B from Knudsen measurements are given in the second and third columns, respectively, and from torsion measurements in the fourth and fifth columns, respectively.

Toward thermodynamic analysis of the vaporization data on $K_2S_2O_5$, Gibbs energy functions of $K_2S_2O_5(s)$ were estimated by methods described elsewhere;[16,17] those for $K_2SO_4(s)$ and $SO_2(g)$ were obtained from the literature.[18] Third-law and second-law values of ΔH°(298 K) of equation (14) from each of the three experiments by both torsion and Knudsen methods are presented in Table VII. The sixth and seventh columns give third-law values and the eighth and ninth columns give the second-law values.

Agreement between Knudsen and torsion results in Table VII is good. Agreement between second-law and third-law values and among the three experiments is poor. A likely explanation of the variation among these results is irreversibility of equation (14) under the conditions present in the Knudsen cell. The very large scatter in the log P vs/T relationship from the third experiment is in line with this explanation. Under such irreversibility the pressure measured would be largely determined by the rate of the forward reaction and by the dimensions of the Knudsen cell and orifices. The rate of the forward reaction might depend on many factors including size of crystals, catalysis by minor impurities, condition of the vaporizing surfaces, etc.

Our conclusion is that neither effusion methods nor any other dynamic method will give dependable vapor pressures from equation (14), unless a method for promoting reversibility can be introduced, e.g., deliberate addition of a catalytic impurity which would have a negligible effect on the equilibrium vapor pressure.[19] For further studies of this system, a static method in which the isothermal partial pressure of $SO_2(g)$ in equilibrium with $K_2S_2O_5(s)$ and $K_2SO_3(s)$ could be adjusted and held for long periods of time probably should be used.

Vaporization of $K_2SO_3(s)$.

Three studies of the vaporization of $K_2SO_3(s)$ were done in the Knudsen-torsion-effusion apparatus in a platinum crucible. Each study was independent, with a fresh sample prepared by decomposition of $K_2S_2O_5(s)$, except that the same crucible was used in each. The results are presented elsewhere.[15]

The results showed little univariance in log P vs 1/T plots until the samples had decomposed to $K_2SO_4(s)$. Then the known vapor pressure of K_2SO_4[20] was produced with acceptable accuracy.

The reason for the nonreproducibility of vapor pressures over $K_2SO_3(s)$ was speculated to be that more than one decomposition reaction was involved, that the reactions were nonreversible under conditions present in the effusion cell, and that the rates and relative contributions from the reactions depended on factors such as surface conditions and size of crystals and possible catalysis by impurities and the cell material. Two possible decomposition reactions were hypothesized:

$$2K_2SO_3(s) = K_2SO_4(s) + 2K(g) + SO_2(g) \tag{16}$$

$$4K_2SO_3(s) = 3K_2SO_4(s) + K_2S(s) \tag{17}$$

The product $K_2S(s)$ in reaction (17) then would vaporize to produce K(g) and potassium polysulfides and ultimately to K(g) and $S_2(g)$ as was found in our studies of the vaporization of $K_2S(s)$.

To establish the validity of the ideas above, studies of the vaporization of K_2SO_3 in the Nuclide mass spectrometer from an alumina crucible were done. The experiments consisted of 18 mass spectrometer scans at crucible temperatures ranging from 700-950°C. The ratio of I_{48}/I_{64} was noted and relative intensities of ions corresponding to K^+ and SO_2^+ as well as other possible vapor molecules such as S_3^+, S_4^+, K_2S^+, and $K_2S_2^+$ were noted.

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Little functional relationship between crucible temperatures and ionic intensities was found. There was a tendency for intensities to decrease with time. Throughout the experiment, no evidence of ions from any vapor molecules other than K^+ and SO_2^+ was found. The ratio of I_{48}/I_{64} was within 0.75 ± 0.25 an observation which indicated that no S_2^+ was present at m/e = 64. No polymeric sulfur ions were observed. The intensity of K^+ was 3-20 times the combined intensities of SO^+ and SO_2^+. The latter effect could have been due to effects of ionization cross sections and unaccounted fragmentation of SO_2^+, as well as chemical effects.

This series of mass spectrometric experiments on K_2SO_3 in alumina indicated that only reaction (16) occurred. The lack of close dependence of ionic intensities on crucible temperature supported the idea that the rate of decomposition depended on additional factors and was not reversible under conditions in the effusion cell. Again as was the case with $K_2S_2O_5$ the rate of vaporization would be determined by the rate of decomposition of K_2SO_3. Dependable vapor pressures of K_2SO_3 cannot be obtained by effusion or other dynamic methods unless a method for promoting reversibility can be introduced.[19]

Mass Spectrometry of K_2SO_3 in Graphite.

Because results by J. E. Bennett at Arkansas State University indicated that vaporization of K_2SO_3 could be studied successfully in graphite crucibles, we undertook a mass spectrometric study of K_2SO_3 in a high-density graphite crucible. As will be seen from the results, the occurrences during vaporization of K_2SO_3 in graphite are significantly different from those when the vaporization is from platinum.

In this set of experiments the shutterable intensities of peaks at m/e values of 39(K^+), 41(K^+), 48(SO^+), 64(SO_2^+ and S_2^+), 65(SO_2^+ and S_2^+), and 66(SO_2^+ and S_2^+) were measured at several temperatures. In addition, at each temperature, a scan of the unshuttered mass spectrum was made at each temperature.

The results of the intensity measurements are reported in Table VIII. The first column gives the temperature range over which the measurements were made (small temperature fluctuations produced the range), and the second through seventh columns give shutterable intensities at the m/e values indicated.

In the last scans of the spectrum, at 713-714°C and at 774°C, peaks corresponding to KS^+, KS_2^+, K_2S^+, $K_2S_2^+$, and $K_2S_3^+$ were observed. In the last scan they had intensities relative to that at m/e = 64 being set at 100 of 3.9, 4.6, 1.1, 1.9, and 1.1, respectively. Uncertainties in these numbers are estimated at ±50%.

The low values of I_{48}/I_{64} in Table VIII, as well as observation of the potassium sulfide and polysulfide ions establish that the vaporization reaction of K_2SO_3 in graphite is different from that in platinum. Apparently, the vapor in graphite contains a high fraction of S_2(g), and then a source of K_2S_x grows in. Perhaps reaction (17) contributes along with a reaction equivalent to the vaporization reactions of K_2S discussed earlier in this report. The condensed potassium sulfide would become sulfur rich until it vaporized congruently, perhaps with K_2S_x species produced as part of the congruent vapor.

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Table I. Summary of Heating Experiments on Cerac K_2S.

Expt.	Crucible	Temp.(°C)	Furnace	Observations of Residual Sample	Observations of Crucible
1	Boron nitride	900	Induction	No sample remaining. Possibly all vaporized.	No chemical attack. Some blistering.
2	Boron nitride	800	Induction	No sample remaining. Should not have vaporized at this temperature.	No chemical attack. Some blistering. Mass increased.
3	Tungsten	700	Induction	Not K_2S. Melted. Gave X-ray lines of $3K_2S \cdot K_2SO_4$ and unidentified lines. K in effusate.	No chemical attack. A black layer observed on the lid around the orifice.
4	Graphite	700	Induction	Sample crept out of the crucible around the lid. Sample melted. X-ray lines not those of K_2S. K in effusate.	No chemical attack.
5	Tungsten	800	Induction	Same as at 700°C.	Same as at 700°C.
6	Graphite	800	Resistance	Same as at 700°C.	Same as at 700°C.
7	Platinum	750	Induction	Additional lines in the X-ray pattern not of K_2S. K in effusate.	Thin, dark layer on inner surface.

Table II: X-ray Diffractograms of White Fraction and Orange Fraction from Preparation of $K_2S(s)$

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White Fraction		Orange Fraction	
d/Å	I/I_o	d/Å	I/I_o
		4.558	5
4.291	80	4.266	80
3.663	70	3.692	60
		3.426	90
		3.248	20
		3.107	10
		2.916	5
		2.773	5
		2.680	5
		2.615	100
		2.510	5
2.449	100	2.452	30
2.235	10	2.406	20
		2.216	10
2.143	10	2.137	10
		1.996	5
		1.971	5
		1.880	5
1.857	20	1.850	10
		1.768	5
		1.718	5
1.684	5	1.698	5
		1.653	5
		1.624	5
		1.593	5
		1.547	5
1.517	30	1.511	60
		1.424	5
		1.406	5
		1.336	5
1.310	10	1.309	10
		1.254	5
		1.240	5
1.172	10	1.171	10
		1.130	5
		1.092	5
		1.068	5
		1.038	5
		1.026	5
		0.989	5
		0.963	10
		0.926	5
		0.872	5
		0.827	5
		0.790	5

Table III

Heating Experiments on Various Crucibles Containing K_2S from Combination of the Elements

Crucible Material	Temperature	Observations of Residue	Observations of Crucible
Inconel	780°C	No X-ray lines of K_2S. Potassium in effusate.	Crucible lost 13 mg.
Nickel	800°C	Effusate dissolved and analyzed; amount of potassium matched total mass loss of sample. No X-ray lines of K_2S. Potassium in effusate.	Crucible lost mass.
Platinum	850°C	No X-ray lines of K_2S. Red and brown deposits in crucible contained both K and Pt. Potassium in effusate.	Crucible lost 27 mg.
Tungsten	780°C, 0.5 hr.	K_2S X-ray lines + additional weak lines. Potassium in effusate.	Crucible lost 8.3 mg.
	780°C, 2 hr.	K_2S X-ray lines + additional weak lines. Potassium in effusate.	Crucible lost 12.9 mg.
	850°C, 1 hr.	Small amount of K_2S + another unidentified phase. Potassium in effusate.	Crucible lost 10 mg.
	900°C, 0.5 hr.	Small amount of K_2S + another unidentified phase. Potassium in effusate.	Crucible lost 24.8 mg.

Table IV: K_2S_2 Calculated d-spacings Compared with Additional Lines from Heating Experiments.

	Calculated		K_xS* from Alumina		$K_{1.4}S$ from Graphite		$K_{1.7}S$ from Zirconia	
hkℓ	d/Å	I/I_o	d/Å	I/I_o	d/Å	I/I_o	d/Å	I/I_o
100	8.49	0						
001	5.84	0						
101	4.573	11	4.55	10	4.607	20		
110	4.245	84	4.25	75	4.318	90	4.282	80
200	3.676	0			3.731	80	3.701	80
111	3.434	210	3.42	125	3.466	100	3.430	80
201	3.111	63	3.11	50	3.123	80	3.107	40
002	2.920	11	2.90	75	2.909	30	2.898	60
210	2.779	21	2.77	50	2.792	40	2.779	20
102	2.713	0					2.736	20
211	2.670	21						
300	2.451	165	2.45	100	2.461	90	2.451	50
112	2.405	106	2.40	75	2.411	90	2.390	50
202	2.286	0						
301	2.160	0						
220	2.122	3						
310	2.039	5						
212	2.013	10						
221	1.995	27	1.99	50	1.998	50	1.996	20
003	1.946	0						
311	1.925	0						
103	1.885	18			1.884	40		
302	1.877	3						
400	1.838	0						
113	1.769	25	1.76	40	1.771	40	1.765	10
401	1.753	0						
203	1.720	0						
222	1.717	40					1.698	20
320	1.687	0						
312	1.672	7						
321	1.620	19			1.623	20		
410	1.604	0						
213	1.594	13						
402	1.555	0	1.55	25	1.548	30		
411	1.547	21						
303	1.524	0						
500	1.470	0						
322	1.460	3						
004	1.460	0						
223	1.434	8						
104	1.432	0						
501	1.426	9						
330	1.415	20						
313	1.408	20	1.40	50	1.406	60	1.407	10
412	1.334	35						

*x not measured

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Table V: Free Energy Functions
$\Phi° = -[G°-H°(298K)]/T$ (J/mol K)

T/K	K(g)	S_2(g)	K_2S(s)	K_2S_4(ℓ)	$\Delta\Phi°$ React.(6)	$\Delta\Phi°$ React.(7)
900	169.3	243.1	149.5	247.3	110.8	144.4
1000	170.8	245.7	155.7	260.3	110.4	143.2
1100	172.2	248.2	162.1	272.7	109.6	142.0
1200	173.6	250.5	168.7	284.6	108.5	140.9
1300	174.8	252.6	175.1	294.6	107.2	140.1

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Table VI: X-ray Diffractograms of K_2S Residues from Experiment in Alumina Crucibles

Left Crucible		Right Crucible	
d/Å	I/I_o	d/Å	I/I_o
4.568	10		
4.273	90	4.256	90
3.696	70	3.698	90
3.415	80	3.430	5
3.099	30		
2.973	5	3.008	5
2.780	5	2.824	5
2.674	5		
2.606	100	2.607	100
2.552	5		
2.502	5		
2.444	40	2.443	5
2.401	40	2.403	5
2.226	20	2.224	50
2.132	10	2.124	50
2.086	5		
1.985	5		
1.919	5		
1.877	5		
1.846	40	1.844	75
1.768	5		
1.713	5		
1.691	5	1.694	30
1.650	10	1.649	30
1.617	5		
1.590	5		
1.541	5		
1.507	70	1.507	80
1.422	5	1.421	25
1.405	5		
1.305	20	1.305	40
1.246	5	1.248	25
1.232	5	1.230	25
1.168	40	1.167	40
1.127	5	1.127	5
1.089	5	1.113	5
1.066	5	1.064	10
		1.034	5
0.991	10	0.993	25
		0.946	5
0.912	5	0.913	5
0.874	10	0.873	10
0.828	5	0.828	10
0.790	5	0.790	10

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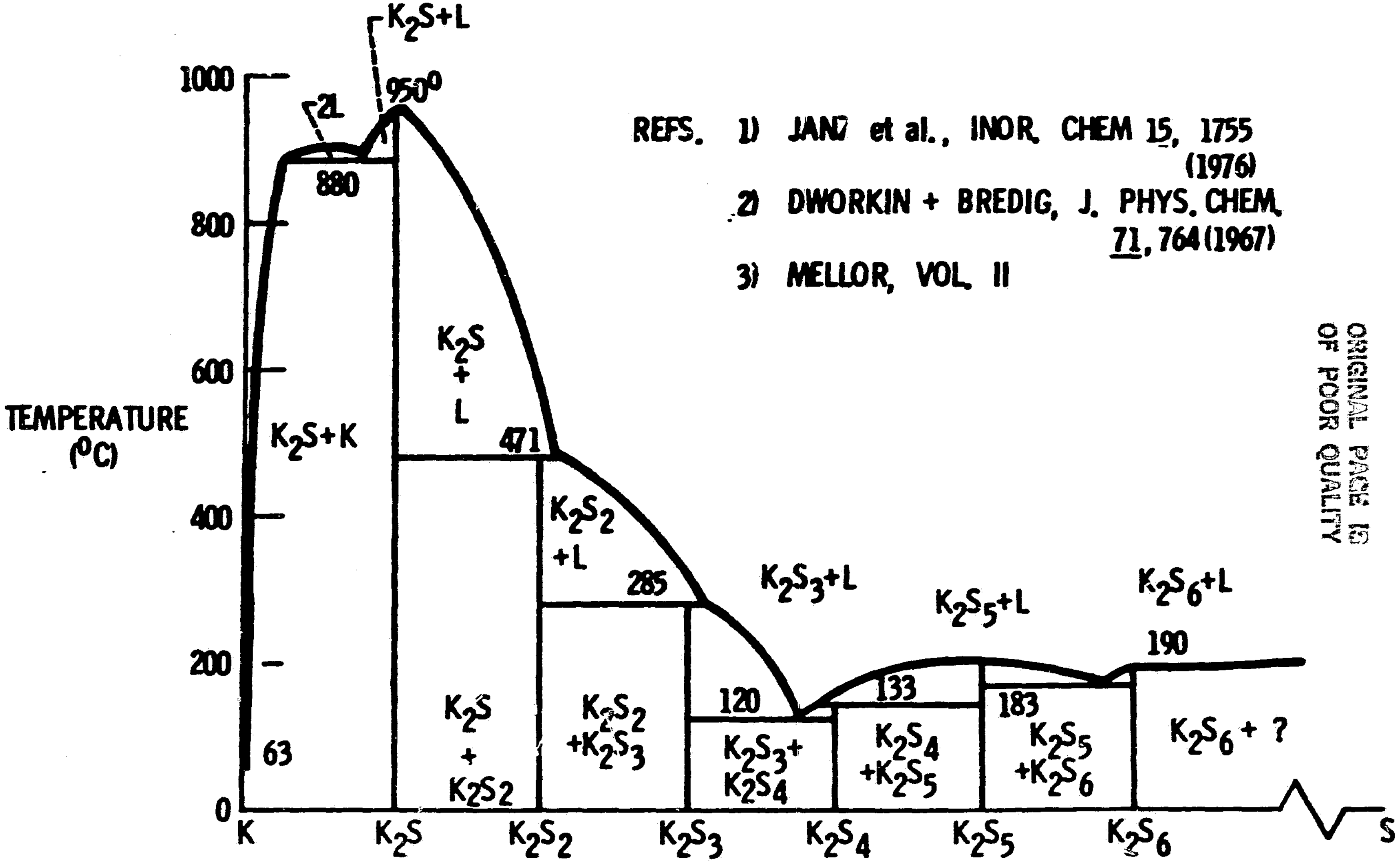
Table VII: Thermodynamic Results from Experiments with $K_2S_2O_5$ in Pt Crucibles. ΔH°(298 K) in kJ/mol.

	Third-Law		Second-Law	
Experiment	Knudsen	Torsion	Knudsen	Torsion
1	106.4±0.2	105.5±0.1	99.6±4.3	101.3±3.3
2	109.6±0.4	108.4±0.4	82.1±13.5	80.5±10.7
3	113.1±0.6	112.7±0.6	73.8±32.0	65.5±27.5

Table VIII: Mass Spectrometric Shutterable Relative Intensities of Ions from the Heating of K_2SO_3 in an Alumina Crucible.

	Intensities Relative to that at m/e = 64					
T(°C)	39	41	48	64	65	66
505	40.0					
507			2.7	100	2.4	8.6
655			1.3	100	1.4	6.7
649	25.2	1.7				
666			3.1	100	1.9	10.7
672	52.5	4.1				
719			3.6	100	1.6	8.8
714	93.4	6.3				
628			1.3	100	1.4	9.5
624	40.7	3.3				
713	65.2			100		
714	59.9	5.3	2.7	100	1.7	8.9
774	92.0	6.7	4.1	100	1.5	7.6

FIGURE 2. **K-S PHASE DIAGRAM**



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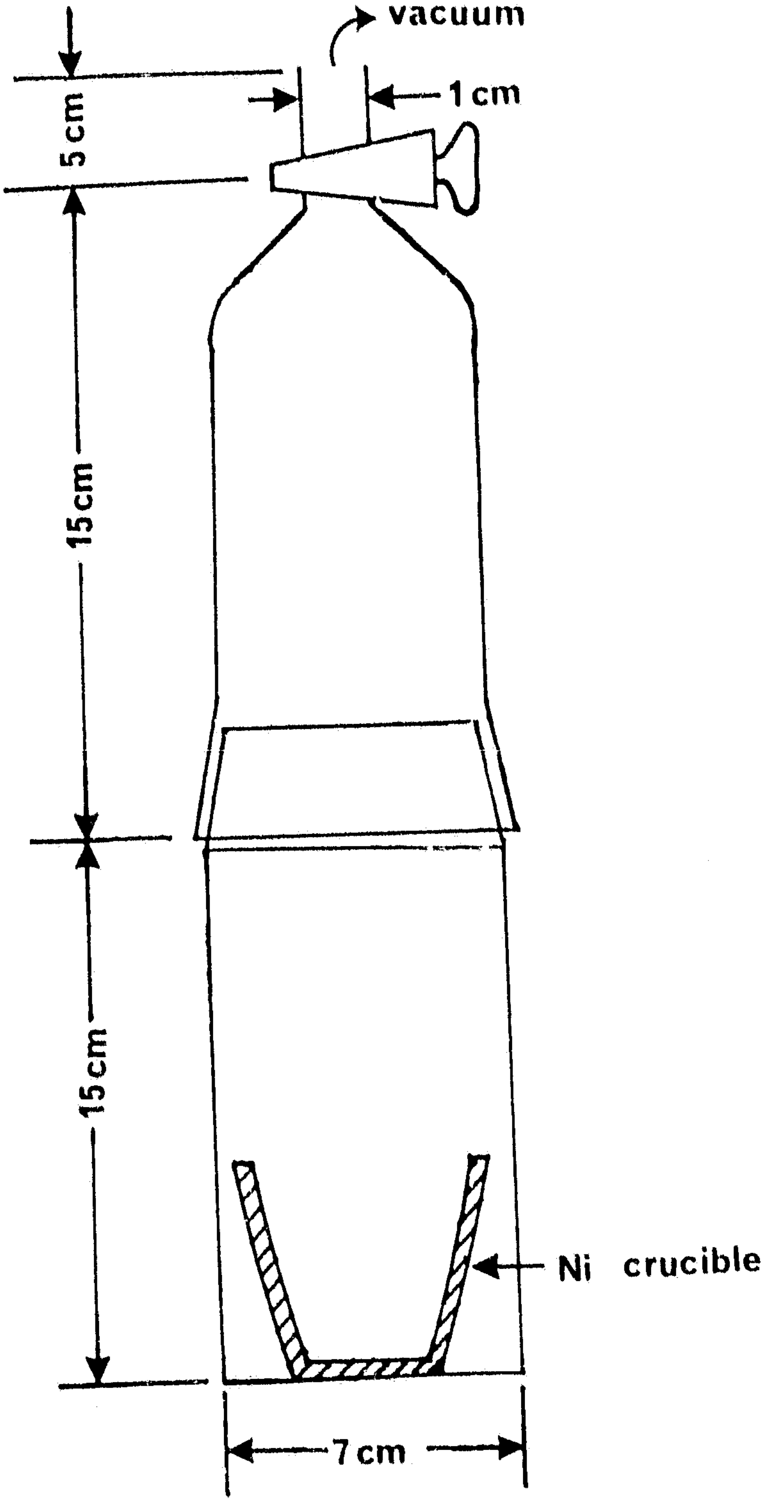
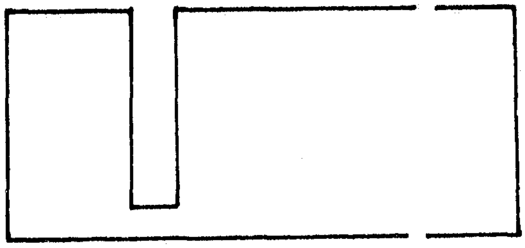
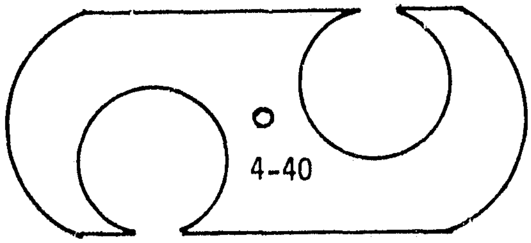


Figure 2. Apparatus for Preparation of K_2S



Side View

Scale



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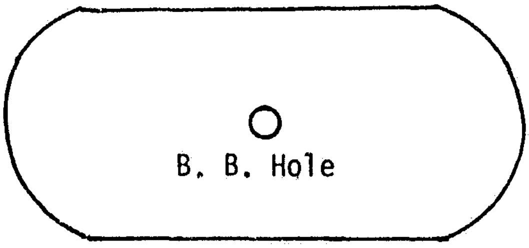

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Figure 3: Graphite Holder for Alumina Cells in Torsion-Effusion Assembly.

FIGURE 4.

TORSION EFFUSION VAPOR PRESSURES OF K_2S

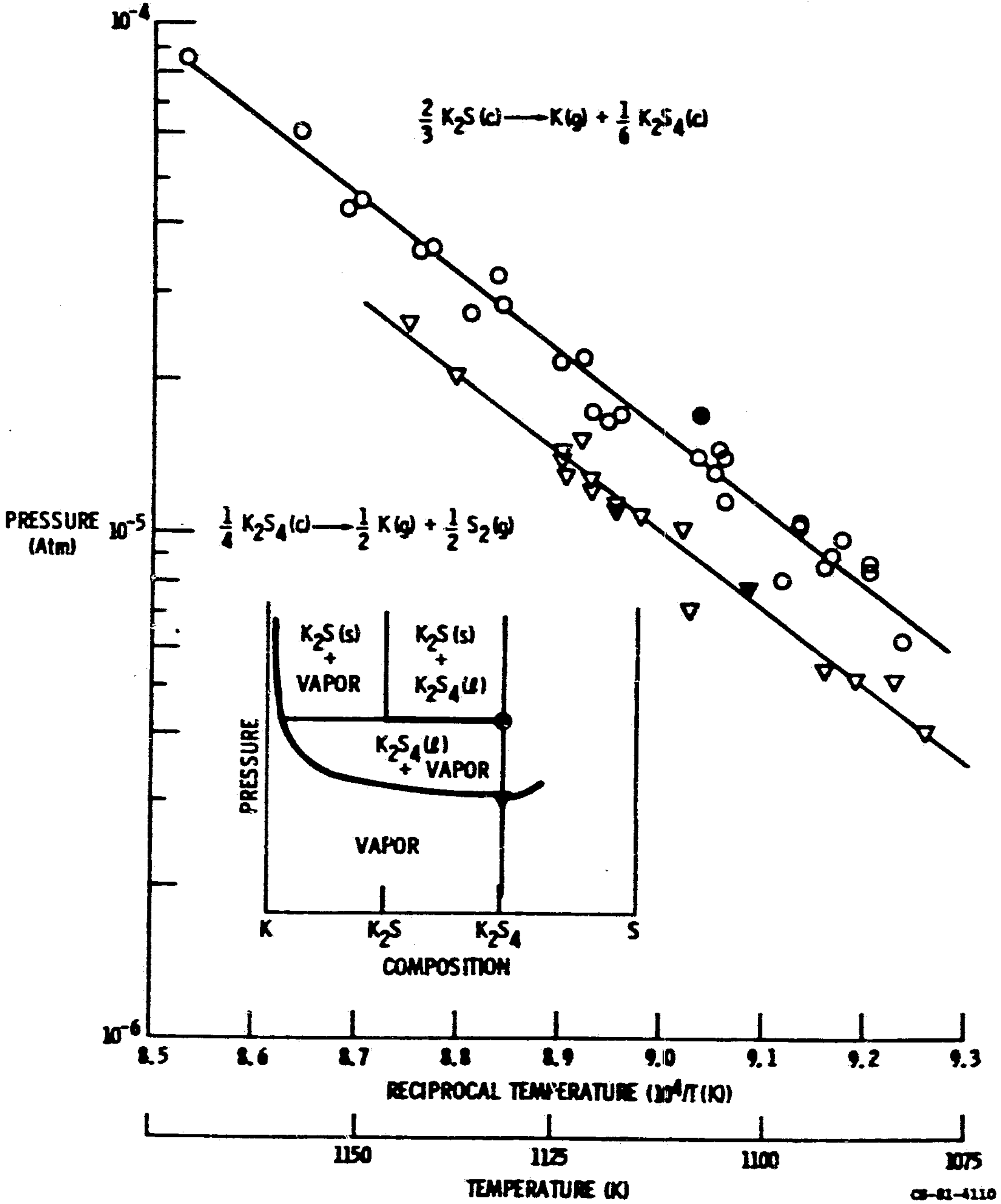

Figure 5. Vapor Pressures by Torsion-Effusion.
Second Experiment in High-Density Graphite.

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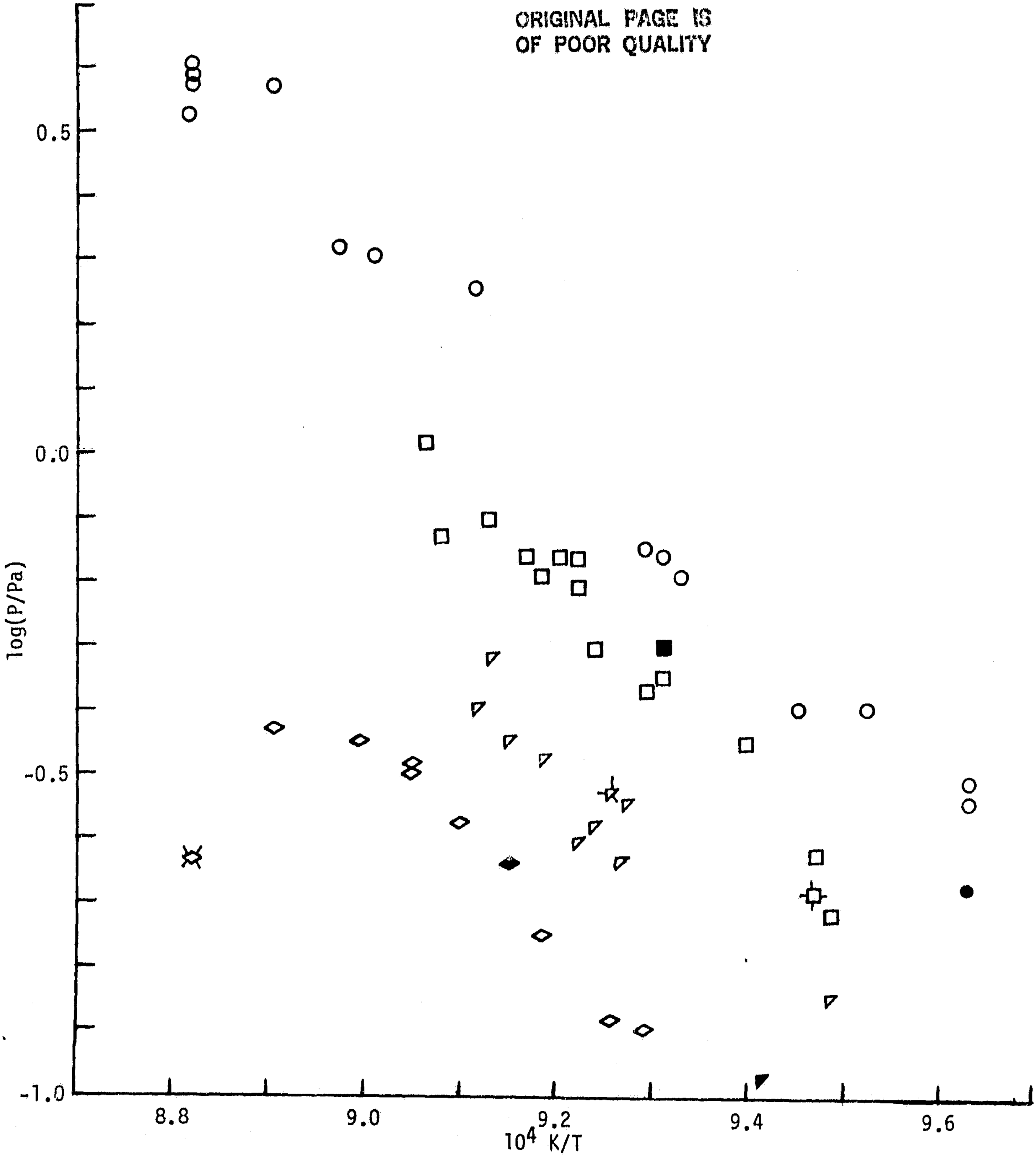

Figure 6. Vapor Pressures by Torsion-Effusion.
Experiment with Alumina Crucibles

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