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AN APPARATUS FOR COMBINED WEIGHT LOSS
AND TORSION EFFUSION STUDIES, AND THE
VAPOR PRESSURES OVER BORON SULFIDE

(M.S. Thesis)

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AN APPARATUS FOR COMBINED WEIGHT LOSS AND TORSION EFFUSION STUDIES,
AND THE VAPOR PRESSURES OVER BORON SULFIDE

by

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ABSTRACT

An apparatus has been constructed capable of providing continuous and simultaneous weight loss and torsion effusion vapor pressures. The torsion pressures can be combined with the weight loss values to provide estimates of the molecular weights of the effusing vapor. The vapor pressure of solid zinc has been measured in the 290 to 330°C. range and the results of this study used to evaluate the performance of the apparatus. Boron sulfide has been prepared, analyzed, and the vapor pressure over its condensed phase measured in the temperature range of 512 to 591°C. and the pressure range of 4×10^{-4} to 7×10^{-3} Torr. Three distinct processes were found to occur in this range.

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INTRODUCTION

A study of Greene and Gilles¹ has resulted in the discovery of gaseous high molecular weight polymeric boron sulfide molecules over glassy sulfur-rich boron sulfide, B_2S_3 . The sample was prepared by the thermal decomposition of metathioboric acid HBS_2 at temperatures below $300^\circ C$. in vacuum. The HBS_2 was formed by the reaction of hydrogen sulfide with elemental boron at $700^\circ C$. in silica tubes.

Mass spectrometric studies of B_2S_3 were carried out by these investigators between 300 and $600^\circ C$. using a Nuclide Analysis Associates 12 inch radius, 60° sector magnetic field mass spectrometer. The boron sulfides found were in three series with molecular weights up to 850 mass units. The first series contained boron and sulfur only while the second and third series probably contained silicon and oxygen in addition, respectively.

More recently, Edwards, Wiedemeier, and Gilles² undertook a mass spectrometric investigation of the decomposition of HBS_2 to B_2S_3 at temperatures below $100^\circ C$. The primary aim of the investigation was to identify (1) the molecules in the gas phase and (2) their fragmentation reactions which occur in the electron bombardment source of the mass spectrometer.

Neither of the above vaporization studies on B_2S_3 or on HBS_2 involved any total pressure measurements. Such information would be useful for the calculation of thermodynamic heats of vaporization and, in the case of HBS_2 , for the determination of the equilibrium constant

for the decomposition reaction. Furthermore, the mass spectrometric results could be combined with total pressure information to give partial pressure data.

Therefore, the purpose of this work was to construct and evaluate an instrument by which total pressure data for boron sulfide and similar substances could be obtained. Such an instrument would also make it possible to obtain accurate thermodynamic data in the case of congruently, or nearly congruently, vaporizing systems.

The instrument constructed is a combined vacuum balance and torsion effusion apparatus which operated simultaneously with the same sample. The advantage of this instrument is that it provides vapor pressures and estimates of the molecular weights of the vapors studied in a continuous experiment over a wide range of temperature and pressure. Second Law heats of vaporization can be obtained by both techniques simultaneously by means of a plot of $\log$ (weight loss rate times the square root of the temperature) and $\log P$ versus the reciprocal temperature.

The experimental apparatus was tested by studying the vapor pressure of a known system, in this case, zinc, and then employed to study the vapor pressure over the condensed phase of B_2S_3 .

CHAPTER I

THEORETICAL

1.1 Knudsen Effusion Method

The most widely used method for obtaining equilibrium vapor pressures in the 10^{-2} to 10^{-6} Torr range is the Knudsen effusion method. This method, founded upon the assumptions of the kinetic theory of gases, utilizes the rate of flow of a vapor through an orifice from a volume saturated with the vapor.

The kinetic theory of gases³ indicates that in a closed system, the number of molecules striking the walls of the container per square centimeter per second is:

$$v = n'\bar{v}/4 \quad (1.1)$$

where n' is the number of molecules per cm.³, and $\bar{v}$ is the mean velocity of the gaseous molecules. The mean velocity is obtained by multiplying each velocity by its probability and integrating over all velocities which results in the relationship,

$$\bar{v} = (8RT/\pi M)^{1/2} \quad (1.2)$$

and the substitution of this equation in equation 1.1 provides a temperature relationship to the number of collisions per square cm. per second:

$$v = n'(RT/2\pi M)^{1/2} \quad (1.3)$$

If a is the area of a hole (orifice) in the walls of the container, and t is any chosen time, then the number of particles striking this orifice in this time t is:

$$v_{a,t} = n'at(RT/2\pi M)^{1/2} \quad (1.4)$$

The mass of particles w striking the area a in time t equals the number of particles times their molecular weight M , hence:

$$w = Mn'at(RT/2\pi M)^{1/2} \quad (1.5)$$

The gas law relates the pressure of a gas to its concentration c and temperature T :

$$P = cRT \quad (1.6)$$

where $c = n/v$, n being the number of moles in volume V .

As n' in equation 1.1 represents the concentration of the gas under consideration, the gas law may be written:

$$P = n'RT \quad (1.7)$$

Substitution of equation 1.7 in equation 1.5 provides:

$$w = (P/RT)Mat(2\pi RT/M)^{1/2} \quad (1.8)$$

which rearranges to the Knudsen effusion equation⁴:

$$P_k = (w/at)(2\pi RT/M)^{1/2} \quad (1.9)$$

The term P_k is used in this study to describe those pressures obtained from Knudsen effusion experiments.

In order to relate pressure to the weight loss rate using the above equation, a number of assumptions had to be made. They were:

(1) that the vapor is effusing from a container in which it is in equilibrium with the condensed phase; (2) that the molecular weight of the vapor is known; (3) that the pressure outside the container is negligibly low, hence no back flow; (4) that the flow through the orifice is free molecular flow; and (5) that the orifice has no length (i.e. is infinitely thin).

In most instances the first four of the above assumptions are realized to a reasonable degree, but it is difficult, if not impossible, to obtain infinitely thin orifices; usually the lengths of the orifices are appreciable. The finite length of the orifice results in restricted flow of the molecules caused by the reflection of these molecules back into the container and, therefore, necessitates a correction factor. This correction term, called the Clausing factor W^5 , can be calculated for cylindrical orifices from an empirical form as stated by Kennard.⁶ For l/r (length to radius) values from 0 to 1.5:

$$W = 1 / \left[1 + 0.5(l/r) \right] \quad (1.10)$$

and for l/r values greater than 1.5:

$$W = \left[1 + 0.4(l/r) \right] / \left[1 + 0.95(l/r) + 0.15(l/r)^2 \right] \quad (1.11)$$

More recent and more accurate values of this correction factor can also be found in the tabulations of W. C. DeMarcus⁷ and of Schultz and Searcy.⁸ The introduction of the Clausing correction factor modifies the Knudsen equation to the form:

$$P_k = (w/atW)(2\pi RT/M)^{1/2} \quad (1.12)$$

Practically speaking, it is sufficient that the orifice diameter be at least ten times smaller than the mean free path of the effusing molecules in order to insure free molecular flow.

The pressures obtained from the Knudsen equation represent the pressure inside the container which, due to the constant loss of material from the container, is less than the equilibrium pressure.⁹ The equilibrium pressure can be related to the Knudsen pressure by:

$$P_{eq} = P_k(1 + aW/\alpha_c A) \quad (1.13)$$

where A is the sample area, a is the orifice area, W its Clausing factor, and α_c the condensation coefficient, defined as the fraction of molecules striking the sample that condense. This relationship can be derived from the Knudsen equation written in a slightly different form:

$$P_k = (dn/dt)(1/aW)(2\pi RTM)^{1/2} \quad (1.14)$$

where dn/dt is the number of moles leaving the orifice per unit time.

If the cell were completely open, i.e. free evaporation from the sample directly (so called Langmuir evaporation), then this equation could be written as:

$$P_l = (1/A)(dn/dt)(2\pi RTM)^{1/2} \quad (1.15)$$

The Langmuir evaporation coefficient is defined as the ratio of the Langmuir pressure to the equilibrium pressure:

$$\alpha_l = P_l/P_{eq} \quad (1.16)$$

where A is the area of the sample. The number of molecules that pass into the gas phase from a sample, irrespective of its container, per unit time is assumed to be

$$dn/dt = \alpha_1 P_{eq} A (2\pi RTM)^{-1/2} \quad (1.17)$$

The number of molecules that leave the gas phase from a Knudsen type container is equal to the sum of those that pass through the orifice and those that strike the sample and condense:

$$dn/dt = aWP_k (2\pi RTM)^{-1/2} + \alpha_c AP_k (2\pi RTM)^{-1/2} \quad (1.18)$$

Under steady state conditions, the number of molecules entering the gas phase, as described by equation 1.17, is equal to the number leaving the gas phase, as described by equation 1.18, i.e.

$$\alpha_1 P_{eq} A (2\pi RTM)^{-1/2} = aWP_k (2\pi RTM)^{-1/2} + \alpha_c AP_k (2\pi RTM)^{-1/2} \quad (1.19)$$

$$\text{dividing by: } (2\pi RTM)^{-1/2}$$

$$\text{yields: } \alpha_1 P_{eq} A = aWP_k + \alpha_c AP_k \quad (1.20)$$

Assuming that the Langmuir evaporation coefficient is equal to the condensation coefficient, and dividing by the condensation coefficient yields:

$$P_{eq} A = aWP_k / \alpha_c + AP_k \quad (1.21)$$

and rearranging yields equation 1.13 as stated above.

Even more sophisticated studies on the relationship between condensation coefficient, crucible dimensions, and vapor pressures have been made, most notably the studies of Whitmen¹⁰ and of Motzfeldt.¹¹ In most cases, however, other factors, such as cell parameters and temperature measurement, introduce errors much greater and, therefore, do not require such refined correction factors.

In the present study only the simplest of the equations have been used, primarily since the condensation coefficient was unknown, and the errors in the other variables were sufficiently large as not to necessitate cell corrections.

The primary limitation of the Knudsen effusion method is that it requires knowledge of the molecular weight of the effusing vapor species. In some instances the vapor may be a mixture, in which case an apparent molecular weight (M^*) may be calculated,¹² if the proportions of the mixture is known, e.g.:

$$M^* = (1/\sum m_i M_i^{-1/2})^2 \quad (1.22)$$

where m_i is the mass fraction of the i^{th} vapor species and M_i is its molecular weight. The Knudsen effusion equation would then have the form:

$$P_k = (w/atW)(2\pi RT/M^*)^{1/2} \quad (1.23)$$

In those cases, however, in which the molecular weight, or apparent molecular weight, is not available, this method cannot be used.

1.2 Torsion Effusion Method

An alternative to the Knudsen effusion method is the torsion effusion method in which vapor pressures are measured directly by a simple dynamic technique. This technique, whose development is attributed to Volmer,¹³ utilizes a measure of the momentum recoil which can be directly related to vapor pressure. In this case the material is allowed to effuse from a crucible suspended in such a fashion that the recoil of the effusing molecules applies a torque on the crucible. In the more common arrangements, a crucible is suspended from a torsion fiber and has orifices placed off center, perpendicular to the axis of the torsion fiber. The angular displacement of the crucible turning against this fiber can be related to pressure by the equation:

$$D\phi = (\sum a_i q_i) P_t f / 2 \quad (1.24)$$

where D is the torsion constant of the suspension fiber in dyne cm./radian, ϕ is the angular displacement in radians, a_i is the area of orifice i , q_i is its lever arm, P_t the torsion pressure, and f a correction factor for finite orifice lengths, similar to the Clausing factor. This factor has been derived by Searcy and Freeman¹⁴ and can be obtained from the form:

$$1/f = 0.0147(1/r)^2 + 0.3490(1/r) + 0.9982 \quad (1.25)$$

$$\text{for} \quad 0 \leq 1/r \leq 2.0$$

More accurate values for this correction factor can be obtained from a recent work of Schulz and Searcy⁸ who have calculated them using more

refined variables.

Since all torsion effusion cells are also Knudsen effusion cells, the results of such experiments can be related to the Knudsen equation--- the torsion pressure being used to calculate the molecular weight (or apparent molecular weight) of the effusing vapor. This can be accomplished by the following relationship, obtained by the rearrangement of equation 1.12 and the substitution of the torsion pressure for the Knudsen pressure:

$$M = 2\pi RT(w/P_t a t W)^2 \quad (1.26)$$

CHAPTER II

EXPERIMENTAL

2.1 Description of Apparatus

The apparatus designed for simultaneous weight loss and torsion effusion measurements was fundamentally simple (Fig. 1). It consisted of a vacuum recording balance, a torsion effusion assembly suspended from the left beam of the balance, and a vacuum line which passes into a furnace. The balance and the vacuum line which contained the effusion apparatus were pumped with a 2 inch air-cooled oil diffusion pump backed by a mechanical vacuum pump. The furnace was of the inductively wound resistance type.

2.1.1 The Balance

The automatic recording balance used in this apparatus was a commercially available Ainsworth type RV-AU-2 (serial #40150) semi-micro vacuum balance. The balance mechanism was of the symmetrical beam type, capable of automatic operation in a vacuum. Small switch weights, totaling 400 mg., suspended from the right stirrup, could be added or removed automatically by a system of cams. Small deflections of the beam, corresponding to small changes in weight, were detected by a variable inductance transducer and fed via a bridge circuit to a chart recorder. The design was such that the maximum allowable beam deflection corresponded to a weight change of 10 mg., this change being recorded on the complete 10 inch span of the chart recorder paper. The switch weights were automatically added or removed when the recorder pen came to either end of its span.

FIGURE 1. VACUUM BALANCE TORSION EFFUSION APPARATUS

The reciprocal sensitivity of the balance was 0.03 mg. with a reproducibility of ± 0.03 mg. and a readability of 0.01 mg. The balance and weight change mechanism were covered by a pyrex bell jar and was connected to the vacuum system via a hole in the base plate directly beneath the left stirrup. Both the bell jar and vacuum connections had "O" ring seals. The balance case stood on a 1 inch thick steel plate which, in turn, sat on five small rubber feet supported on a table bolted to a main building column.

2.1.2 The Torsion Effusion Assembly

The torsion effusion assembly which was suspended from the left beam of the balance was comprised of, in the order from top to bottom, a modified stirrup, a platinum-10% nickel taut-band torsion fiber, a mirror and damping disc assembly, and the torsion crucible and its suspension rod.

2.1.2.1 the stirrup

A modified balance stirrup was constructed to allow rotation of the torsion fiber and assembly without loosening the set screws which hold the fiber. This operation was necessary to allow the mirror, used to measure the deflection of the torsion effusion assembly, to be faced in a direction which was convenient for measurement of its position. The rotation of the fiber was in sixteen steps, each of about 22.5° . The design was sufficiently rigid that the twisting of the fiber did not cause a twisting of the stirrup (Fig. 2).

FIGURE 2 ROTATING STIRRUP

2.1.2.2 the torsion fiber

The fiber was a taut-band strip* made of a platinum-10% nickel alloy. This fiber, specifically designed for use in galvanometer suspensions, is commercially available in a wide range of torsion constants. It was operated under a recommended load of 50g. and did not break when subjected to loads of 250 to 300g. The fibers used in this study were about 80 cm. long, with a cross-section of 0.0006 x 0.006 inch, and had a torsion constant of 12.0 dyne cm./radian/cm. (equal to 0.15 dyne cm./radian for an 80 cm. length). In order to attach the fiber to the stirrup and mirror assembly, it was necessary to glue the ends of the fiber into the bore of fine brass rod. About 1.5 cm. lengths of the rod were used, and the fiber was glued with epoxy cement. The use of a platinum nickel fiber had decided advantages over the tungsten or quartz fibers used by most other workers since the platinum fiber is extremely resistant to oxidation and, as indicated by experiments to be described, need not be recalibrated before each use.

2.1.2.3 the mirror and damping disc assembly

The mirror and damping disc were attached to an aluminum alloy (type 6066-T6) shaft of 11 inch length and $\frac{1}{4}$ inch diameter (Fig. 3). The mirror was attached, with black wax as cement, to a notched portion of the rod such that it was almost in the plane of the axis. This mirror, originally intended for use in galvanometers, was $\frac{5}{8}$ inch in diameter and had a front silvered surface which was ground concave with a one meter focal length.

*Sold by Sigmund Cohn Corp. 121 So. Columbus Ave., Mount Vernon, N. Y.

FIGURE 3 TORSION EFFUSION ASSEMBLY

The damping disc was attached to the same rod as the mirror and was made from iron-free high purity aluminum*. It was 1.5 inches in diameter and 0.15 inch thick. The component parts of this assembly were carefully machined in order to guarantee straightness.

The brass ends of the torsion wire were attached to the upper end of the shaft with two 2-56 brass set screws. The crucible suspension rod was screwed into the bottom end of the shaft.

2.1.2.4 the crucible and its suspension

The crucibles used in these experiments were fabricated from spectrographic grade graphite. They were cubes (Fig. 4) with four separate sample chambers and orifices. The cell was about 2 cm. on each edge with sample chambers of cylindrical cross section 0.7 x 1.5 cm., each fitted with tapered plugs. The orifices were either 0.75 or 1.0 mm. in diameter and about 0.7 mm. thick. The walls in the immediate area of the orifices were thinned to allow for the short orifice length. The accurately measured lever arm of each orifice was about 0.5 cm.

The crucible was suspended from the mirror and damping disc assembly by a 1/8 inch diameter x 12 inch long graphite rod (spectrographic grade) which was threaded at both ends and screwed into the crucible.

The over-all dimensions of the crucible were obtained using a traveling microscope which could be read to 0.001 mm. The orifice area was obtained by first tracing a projection of the orifice outline, utilizing a Leitz "Dialux-Pol" polarizing microscope (serial #611348)

*Type 6101 alloy, having high electrical conductivity, which contains small amounts of Mg and Si, and only trace amounts Fe, Mn, and Ti. It was obtained as a gift from the Dow Metal Products Co., a division of Dow Chemical Corp.

and an Abbe camera lucida projector,⁴³ and then graphically integrating the area of this tracing.

The orifice length, which represented the wall thickness at the point of the orifice, was obtained using the calibrated fine focusing adjustment on the polarizing microscope. The fine adjustment was calibrated by focusing the microscope on both faces of a microscope slide whose thickness had been accurately measured. The microscope was focused on the surface of the crucible at the edge of the orifice and then focused through the orifice on the surface of a closely fitted shaft which had been placed in the cylindrical crucible chamber. The distance between the two points of focus represented the orifice thickness. These latter measurements could be read reproducibly to at least 0.01 mm.

The lever arm of the torsion cell was calculated from external dimensions of the torsion cell. This represented the perpendicular distance from the axis of the cell to a line passing through the orifice perpendicular to the cell face. The radius of the orifice was calculated from the orifice area.

2.1.3 The Vacuum System

The vacuum system served to evacuate both the balance and the torsion effusion region. A 2 inch air-cooled oil diffusion pump and a liquid nitrogen trap served to maintain a pressure which was routinely of 1×10^{-6} Torr as measured with an ionization gauge tube (RCA 1949) and a homemade gauge control. The diffusion pump has a speed of 95 liters/second and is part of a modular pumping system (Veeco) which contains all the necessary valving to allow rough pumping of the system

- NOTE :
1. CENTER HOLE — DRILLED WITH # 32 DRILL AND TAPED NF 6-32 .
 2. SIDE HOLES — THINNED WITH 17/64 END DRILL TO DEPTH OF 1/32" ORIFICE DRILLED WITH 0.75 OR 1.0mm dia. DRILL .
 3. FOUR PLUGS MADE FOR EACH CRUCIBLE — TAPERED, 5/32" LONG , TO FIT IN 3/32" .

FIGURE 4 TORSION CRUCIBLE

without turning off the diffusion pump. This system was backed by a Welch Duoseal Model 1402 mechanical pump with an additional liquid nitrogen trap between the forepump and the diffusion pump.

In the course of experimentation, it was found that the inclusion of liquid nitrogen in the high vacuum trap resulted in only a reduction of pressure from 1×10^{-6} to 8×10^{-7} Torr, so that in most instances the cooling of this trap was neglected.

The vacuum line was made of pyrex and was connected to the balance and vacuum pump using housekeeper glass to metal seals. In the region of the mirror an optical window was attached which was used in an attempt to reduce distortion during measurements of the angular displacement of the torsion apparatus. The tube which contained the torsion cell and which passed through the resistance furnace was made of quartz. The average inner diameter of the vacuum line tubing was 50 mm.

Considerable difficulty was encountered in the construction of the vacuum line. In particular, it was difficult to provide good alignment such that the crucible and torsion effusion assembly did not hang off-center, and, since the component parts of the system were rigid, breakage of the glass occurred on several occasions. It is suggested that the upper part of the vacuum line, if reconstructed, be made entirely of metal with only the furnace tube and its connection made of glass. This would allow the inclusion of bellows connections in the vacuum line which could be easily distorted so as to obtain better alignment of the furnace tube.

2.1.4 The Furnace and Heat Shields

The furnace used in these experiments was a Marshall resistance

furnace, inductively wound, with a series of external taps which allow adjustment of the temperature along the length of the furnace. It had a bore of 2.6 inches and a length of 16 inches. The maximum obtainable temperature was 1200°C . Power for the furnace was obtained from a Wheelco temperature controller. This system included an indicating temperature controller, a DC amplifier and a saturable core reactor. This controller allowed rapid heating to the desired temperature and served to maintain the crucible temperature within 0.1°C . for several hours.

The heat shield assembly was supported from the upper lip of the quartz furnace tube and shielded the crucible from the inductive effects of the furnace. The heat shield plates also served to provide a surface on which the effused material could condense. Hence, there were about a dozen plates placed in the cooler region above the furnace which effectively reduced condensation on the torsion apparatus to such a point that it was not significant in the weight loss measurements. These upper plates were fabricated from aluminum while the ones in the furnace region were made from tantalum. The shield assembly further acted as a support for the thermocouple which was used to measure the torsion cell temperature. The thermocouple was contained in a crucible identical in dimensions and mass to the torsion cell and was placed about 0.5 cm. below it. This arrangement insured that the response time of the reference thermocouple was about the same as that of the torsion cell. The shield assembly was grounded, the ground wire as well as the thermocouple leads passing out of the bottom of the furnace tube via black wax (Apiezon W) sealed capillary tubes. The grounding

was necessary to prevent swinging of the torsion cell when the furnace was operated since the furnace was inductively wound and would couple with the crucible.

2.2 Calibration of Torsion Fibers

Some workers⁴¹ suggest calibrating the torsion fiber against a disc of known moment of inertia, first finding the period of oscillation of the torsion system without the crucible and then the torsion system without the crucible plus an inertia disc. The torsion constant can then be calculated from the relationship:

$$D = 4\pi^2 I_2 / (t_2^2 - t_1^2) \quad (2.1)$$

where I_2 is the moment of the inertia of the disc, t_2 the period of the disc plus torsion assembly, t_1 the period of the torsion assembly only.

Since it seemed apparent that the torsion constant of the fiber might change value with changes in load, it was decided that in these experiments several discs of known moment of inertia be used whose mass approached that of the crucible, and that the periods of these discs plus torsion assembly be compared to each other rather than to the torsion assembly alone. In this case the torsion constant is calculated using the relationship:

$$D = 4\pi^2 (I_3 - I_2) / (t_3^2 - t_2^2) \quad (2.2)$$

where I_3 , I_2 , t_3 , and t_2 are the moments of inertia and periods of rotation of the different discs respectively. Better agreement was formed between the discs as compared to each other than between the discs as compared to the torsion apparatus, indicating that the change

in load causes some small change in the torsion constant of the fiber. This change is shown in table 1. The first column in this table identifies the disc; the second, its diameter; the third, its mass; the fourth, its moment of inertia; the fifth, its period of oscillation; the sixth, the torsion constant of the fiber as calculated by using equation 2.1; the seventh, the torsion constant as calculated from equation 2.2, where I_3 and t_3 refer to the large disc; and the last, the torsion constant as calculated for column 7, except I_2 and t_2 refer to the small disc.

TABLE 1
Torsion Constant Calculations

Name	Dia. (inch)	Mass (grams)	I (g. cm. ²)	Period (sec. $\pm$ 0.02)	D (vs. App)	D (vs. 1d)	D (vs. sd)
Apparatus			no disc	94.70	X	X	X
Large Disc	1.625	12.6864	24.958	122.27	0.16476	X	X
Medium Disc	1.500	10.9417	18.128	115.34	0.16513	0.16379	0.16375
Small Disc	1.250	7.8995	8.750	105.08	0.16660 0.165 $\pm$ 0.001	0.16376 0.16377 $\pm$ 0.00002	X

The moment of inertia of the torsion assembly itself does not appear in the above equations but it can be calculated both from the dimensions of the torsion assembly, which yields a moment of inertia of 37.46 gram cm.², or from the slope of a plot of $t_1^2/4\pi^2$ versus I_1 . The moment of inertia calculated by this latter method was 37.18 gram cm.². These values agree with each other to within one percent, indicating

the correctness of the torsion constants obtained.

The inertia discs consisted of flat aluminum discs 1.25, 1.5, and 1.625 inches in diameter, and 0.125 inch thick with 0.125 inch diameter shafts. These shafts were threaded so that they could be screwed into the bottom of the torsion effusion assembly.

The method used to obtain the period of oscillation was as follows: an inertia disc plus torsion assembly was set oscillating by passing a magnet near the damping disc and then removing it. The magnitude of the oscillation was usually 180° each side of the center. The assembly was allowed to oscillate for five complete oscillations, the time being measured to 0.1 second with an electric timer. The period was measured from the center point of the oscillation using the projector and scale as the indicating device (Fig. 3). Depending upon the size of the disc and length of the fiber being calibrated, the time for five complete oscillations ran from 500 to 1000 seconds and could be measured reproducibly to 0.1 second.

Considerable advantage was obtained by using the platinum-10% nickel taut-band strip as the torsion fiber instead of the more usual tungsten or quartz fibers. This alloy is chemically more resistant than the others and consequently, its torsion constant remains unchanged for long periods of time, even when under load and exposed to the atmosphere. For example, the torsion constant of fiber #3 was first found to be 0.1590 ± 0.0004 dyne cm./radian, and after four months of use, it was found to be 0.1582 ± 0.0002 dyne cm./radian, a change of less than one percent.

Another advantage is that these fibers are supplied by the manufacturers fully annealed and consequently the rest point of the fiber

is very stable. For example, during the Boron Sulfide Run #1, the zero point remained constant with a scale reading of ± 0.1 cm. for a period of several weeks during which the sample was heated and cooled each day.

The fiber was never allowed to become hot during the course of an experiment. This was accomplished by the placing of heat shields above the furnace and, since the torsion fiber was separated from the crucible by the torsion assembly and the graphite crucible support rod, there was little opportunity for it to be heated by radiation or conduction.

As described previously the fiber was glued into the end of a small brass rod, 0.062 inch in diameter, with a 0.010 hole drilled axially to a depth of 0.25 inch. The fiber was glued with a commercial variety of epoxy cement. The small bore of the hole assured that the fiber was axially aligned. Because only a very small amount of epoxy cement was required, no outgassing problem was involved.

2.3 Temperature Calibration

The temperature of the torsion cell was measured by determining the output of a chromel/alumel thermocouple placed in a dummy cell located one cm. below the torsion cell. The vertical position of the furnace resulted in a large vertical temperature gradient, probably due to convection currents in the space between the furnace and furnace tube. Some attempt was made to reduce these convection currents by closing the hole around the furnace tube at the top of the furnace with an asbestos sheet. No attempt was made to measure the magnitude of the temperature gradient within the furnace. Since this gradient

appeared to be fairly great, it was necessary to make a calibration of the actual torsion cell temperature in terms of the dummy or reference cell temperature. This was accomplished by placing a fine copper/constantan thermocouple directly into one of the chambers of the torsion cell and leading the thermocouple leads out of the vacuum system via black wax seals. All calibrations were done at a pressure of 10^{-2} to 10^{-3} Torr, which was probably too high a pressure. It is suggested that lower pressures (10^{-5} to 10^{-6} Torr) be used during future calibrations. In the 100 to 300°C. range #30 copper/constantan enameled thermocouple wire was used. This wire was subsequently calibrated by comparing it to the boiling points of water (100°C.), benzophenone (216°C.), and naphthalene (305°C.). The first of the substances is a primary temperature standard, the latter two are secondary standards.¹⁵ In this operation the copper/constantan thermocouple was placed in a sealed glass tube suspended vertically above the calibration substance in an open Kjeldahl flask. This substance was heated until it boiled quite vigorously. That temperature which was constant for a few cm. above the surface of the boiling liquid was accepted as the boiling point of the standard. The boiling point temperature was corrected to normal atmospheric pressure according to the procedure described in Lange's Handbook of Chemistry, 7th Ed., page 856.

The calibration curve obtained in the range from 100 to 300°C. is shown in Fig. 5. Those data points taken during increasing temperature are shown as solid circles, while those taken during decreasing temperature are shown as open circles. The calibration is probably accurate to $\pm 1^\circ\text{C}$.

FIGURE 5 TEMPERATURE CALIBRATION

2.4 Operational Procedure

The samples to be studied were placed in a previously outgassed and weighed torsion cell (outgassed at a temperature of 1000°C . and a pressure of 10^{-6} Torr), the sample being divided between the four cell chambers. The cell and its support rod were then attached to the torsion assembly and the vacuum line was subsequently evacuated to a pressure of about 10^{-6} Torr. After this pressure had been obtained, the sample was slowly heated until a measurable deflection of the torsion assembly was obtained. The temperature was then raised to 10°C ., and the process was repeated. This procedure was continued until the deflection of the torsion assembly was so great that it could no longer be read. Frequently the temperature was then decreased in increments of 5 to 10°C , measurements being taken at each temperature. The deflections were read by employing a galvanometer projector and ground glass scale placed one meter from the mirror in the torsion assembly. This distance was measured using a meter stick to an accuracy of ± 0.2 cm. while the deflections projected on the ground glass scale were read to ± 0.1 mm. (Fig. 3). The projected deflections were twice as great as the rotation of the torsion assembly itself, because the light beam was reflected from the surface of the mirror. The projected deflection angle was calculated using the perpendicular distance from the mirror to the center of the scale and from the distance from the center of the scale to the projected image. The projected deflection angle was then divided by two to give the actual deflection angle. The output of the reference thermocouple was measured using an L & N type 8662 portable potentiometer (serial #1326926) with an ice water

bath as a reference resulting in a precision of $\pm 0.1^{\circ}\text{C}$. The weight loss during the measured periods, as recorded on a chart recorder, could be read to a precision of ± 0.01 mg. The time elapsed between each measurement was obtained employing an electric timer and read to ± 0.01 minute.

The zero point of the torsion apparatus, as measured on the ground glass scale, was determined before the start of a run, and before turning on the furnace at the beginning of each day's run. The zero point reading remained unchanged within ± 1 mm. over a period of a few weeks.

2.5 Errors

The errors in the torsion effusion and Knudsen effusion equations are of two types. The first type is the uncertainty in the measurements of the physical dimensions of the torsion cell, weight change, temperature, deflection angle and torsion constant of the fiber. The second type of error lies in the application of the torsion and Knudsen effusion equations themselves. It is impossible, under the present circumstances, to determine whether or not the systems studied followed ideal behavior.

The uncertainties in the physical measurements for the torsion cell are as follows. The lever arm uncertainty is estimated to be less than 0.5%, assuming that the axis of rotation falls in the exact center of the cell, which is probably justified since no sideways motion was noted in the swinging torsion cell. The orifice area, is known to better than 0.1% and the orifice length to 2%. The resulting errors in the force and Clausing correction factors is therefore 1%. The angular

displacement of the crucible is uncertain from 1 to 15% depending on the magnitude of the deflection, assuming deflections of 1 to 10^0 . The error in the torsion constant is estimated at 0.5%.

Therefore, the uncertainty in the pressures obtained from the torsion effusion equation is in the order of 5 to 20% depending upon the magnitude of the deflection. This does not include the uncertainty in the value of the force correction factor or in the deviation from ideality.

The magnitude of the errors to be found in the Knudsen pressures are essentially the same as for the torsion pressures, and they depend largely upon the accuracy and stability of the temperature measurement and control, and on the mass of sample volatilized. In general, the uncertainty in the Knudsen pressures averages 5 to 10%, assuming weight loss values of 0.5 to 3.0 mg. per measurement.

The resultant uncertainties in the molecular weight calculations, estimated from the relationship $M^* = M(P_K/P_t)^2$ where M is the molecular weight used in the Knudsen pressure calculation, and M^* is the estimated or average molecular weight, varies from 20 to 50%.

The above errors assume no error in the temperature measurement, which depends more upon the individual experiment and are, therefore, treated elsewhere.

CHAPTER III
CALIBRATION AND EVALUATION

3.1 Zinc Calibration

In order to determine whether the apparatus was functioning properly, the vapor pressure curve of zinc was determined. Zinc was used for the following reasons:

1. Its vapor pressure and heat of vaporization are fairly well established by methods which included both Knudsen and torsion effusion methods.
2. Zinc vapor is known to be monatomic.⁴²
3. It has a vapor pressure of 10^{-4} to 10^{-2} Torr in the temperature range of 280 to 340°C . which is easily obtained with the existant furnace arrangement and is in the range of temperature and pressure to be measured in subsequent experiments.
4. Its condensation coefficient is probably very close to one, as it is in the case of most metals.
5. Zinc is easily obtainable in high purity.

The literature covering the vapor pressure of zinc has been thoroughly reviewed by Barrow and co-workers¹⁶ who calculated, using their own data and the data of other workers, both by Second and Third Law treatments, the vapor pressure equations and heat of vaporization of zinc. Their own experimental determinations were carried out using the torsion effusion method. In reviewing the work of others, they considered both the vapor pressures obtained over the solid and over the liquid (m.p. = 319.5°C .).

Three sets of data for the vapor pressure over the solid were considered, namely the work of Vance and Whitman,¹⁷ of McKinley and Vance,¹⁸ who carried out total collection Knudsen effusion experiments, and that of Coleman and Egerton¹⁹ who used Knudsen effusion weight loss. The number of measurements of the pressure over the liquid zinc phase are more numerous, as are the techniques used. Heycock and Lamplough,²⁰ and Leitgeb,²¹ used measurements of the boiling points at atmospheric pressure. Greenwood,²² obtained the vapor pressure using boiling point measurements at 6 to 53 atmospheres. Braune²³ used a transpiration method at low temperatures and a boiling point method at higher temperatures. Boiling point methods were also employed by Rodebush and Dixon.²⁴ Vapor pressure measurements were performed by Jenkins,²⁵ and Baur and Brunner²⁶ who employed manometric methods. A thorough evaluation of both the measurements above the solid and liquid phases indicated that only the pressure measurements above the liquid were consistent and reliable. Barrow, et al. (loc. cit.) took the values of ΔH_{298}° calculated from 69 vapor pressure measurements on the liquid obtained by the above workers and found their mean, weighted them and derived the mean value for the enthalpy of sublimation:

$$\Delta H_{298} = 31.18_0 \pm 0.00_8 \text{ kcal/mole} \quad (3.1)$$

From this value and from selected thermochemical data, they found the following equations for the vapor pressure, in Torr, at $T^{\circ}\text{K}$ of solid and liquid zinc.

$$1. \text{ Above the solid phase:} \quad (3.2)$$

$$\log P = 9.8253 - 0.1923 \log T - 0.2623 \times 10^{-3} T - 6862.5/T$$

2. Above the liquid phase:

(3.3)

$$\log P = 12.4480 - 1.2742 \log T - 6676.4/T$$

3.2 Experimental

Vapor pressure measurements of zinc employing the vacuum-balance-torsion-effusion apparatus were carried out using the procedure described in chapter 2.4. One to two grams of reagent grade granular zinc ("Baker Analyzed" reagent, lot 27169, Assy 99.6% zinc) was placed in the previously outgassed torsion cell. During runs of several days or a few weeks, only a few hundred mg. of the sample were vaporized.

A number of runs were made with zinc, most with uncalibrated torsion fibers. This allowed a general evaluation of the functioning of the apparatus and permitted detection and correction of minor misfunctions of the system. These tests indicated that the torsion effusion apparatus functioned correctly, without interference from the inductive effects of the furnace or from the damping magnet. It also indicated that the log of the deflection bore a linear relation to the reciprocal of the absolute temperature.

The last run made with zinc, i.e. zinc run #18, was carried out using a calibrated torsion fiber and was used to establish the precision of the instrument. The temperature range covered in this run was from 290 to 335°C. with the resulting zinc pressures, corresponding to a deflection of the torsion apparatus of 1.5 to 9.50°, in the range of 7×10^{-4} to 6×10^{-3} Torr. The weight loss rate for the sample varied from 0.6 to 2.0 mg. per hour.

3.3 Results

The vapor pressure data obtained in this experiment are tabulated

in table 3 and are represented in the form of a $\log P$ versus $1/T$ plot in figure 6. All points taken during unstable temperature conditions are omitted. The first six columns in table 3 refer to the torsion effusion measurements. The first column contains the identification of the measurement; the second, the temperature in degrees centigrade; the third, the absolute temperature; the fourth, the reciprocal absolute temperature; the fifth, the angular deflection of the torsion fiber; the sixth, the torsion pressure as calculated from equation 1.24. The last eight columns refer to the Knudsen effusion measurements. The seventh column identifies the two torsion measurements between which the Knudsen effusion measurement was made; the eighth, the average temperature of the measurement period; the ninth, the absolute temperature; the tenth, the reciprocal of the absolute temperature; the eleventh, the mass loss; the twelfth, the elapsed time for the measurement; the thirteenth, the Knudsen pressure calculated from the weight loss rate and the known molecular weight of zinc according to equation 3.4; and the last column, the molecular weight calculated from the average torsion pressure from column 6 and weight loss during the elapsed measurement period, calculated according to equation 1.2.

The parameters of the torsion cell used in the experiments (cell #2) are tabulated in table 2. The first column contains the identification of the orifice whose parameters follow; the second, its area; the third gives the lever arm; the fourth, the orifice length; the fifth, the ratio of orifice length to radius; the sixth, the Clausing factor; and the last, the force correction factor. The latter two

values are taken from the tabulations of Searcy and Schulz.⁸

TABLE 2
Parameters of Torsion cell #2

Orifice #	a_i ($\text{cm.}^2 \times 10^{-6}$)	q_i ($\text{cm.} \times 10^{-4}$)	l_i ($\text{cm.} \times 10^{-3}$)	l/r	W	f
1	0.007706	0.0507	0.117	2.36	0.4760	0.5317
2	0.008030	0.0510	0.116	2.29	0.4830	0.5392
3	0.007901	0.0514	0.137	2.73	0.4421	0.4954
4	0.007831	0.0525	0.122	2.44	0.4682	0.5234

The Knudsen pressure equation which results from the values in table 2 is

$$P_k = 2.43(w/t)(T)^{\frac{1}{2}} \quad (3.4)$$

when w/t is in units of grams/minute and T is degrees Kelvin; the molecular weight of zinc was taken as 65.38.

Besides calculating the vapor pressures of zinc using the Knudsen effusion and torsion equations, Third Law heats of vaporization were calculated from the pressures obtained by both these methods. These calculations were possible since tabulated thermodynamic data for zinc are available providing free energy functions, necessary to obtain the standard enthalpy of vaporization at 298.16°K.

The standard free energy G^0 of a substance at a specific temperature

T is defined in terms of standard entropy and enthalpy:

$$G_T^{\circ} = H_T^{\circ} - TS_T^{\circ} \quad (3.5)$$

The free energy function is obtained by subtracting the enthalpy at 298°K. (ΔH_{298}°) and dividing by the temperature, i.e.:

$$\frac{G_T^{\circ} - H_{298}^{\circ}}{T} = \frac{H_T^{\circ} - H_{298}^{\circ}}{T} - S_T^{\circ} \quad (3.6)$$

These free energy functions can be calculated from heat capacity measurements for the solid and from the partition function determined from spectroscopic data and the Sackur-Tetrode equation for the gas.

The difference between the standard free energy of the vapor and of the condensed state is the standard free energy of vaporization:

$$G_T^{\circ} = G_T^{\circ}(g) - G_T^{\circ}(c) \quad (3.7)$$

which can be written as:

$$\frac{\Delta G_T^{\circ} - \Delta H_{298}^{\circ}}{T} = \frac{G_T^{\circ}(g) - H_{298}^{\circ}(g)}{T} - \frac{G_T^{\circ}(c) - H_{298}^{\circ}(c)}{T} \quad (3.8)$$

This relationship can be further rearranged to:

$$\Delta H_{298}^{\circ} = T \left[\frac{\Delta G_T^{\circ}}{T} - \frac{G_T^{\circ}(g) - H_{298}^{\circ}(g)}{T} + \frac{G_T^{\circ}(c) - H_{298}^{\circ}(c)}{T} \right] \quad (3.9)$$

The free energy functions for a great number of substances are tabulated for each state as a function of temperature and can be found in several standard reference works, namely that of Stull and Sinke²⁷ and Hultgren, Orr, Anderson, and Kelly.²⁸

This free energy function data plus a single experimental pressure at a known temperature can be used to calculate the standard enthalpy

of vaporization (ΔH_{298}°), utilizing the relation

$$G^{\circ}/T = -R \log_e P \quad (3.10)$$

where P is in atmospheres. The free energy functions for zinc were obtained from the tabulations of Hultgren, Orr, Anderson, and Kelly, and the above relationships used to calculate ΔH_{298}° from the pressures obtained in zinc run #18. These values are tabulated in table 4. The first column of this table contains the identification of the measurement; the second, the temperature in degrees centigrade; the third, the absolute temperature; the fourth, the free energy function for the gas as interpolated from the literature;²⁸ the fifth, the free energy functions for the condensed phase obtained in the same manner as those in column four; the sixth gives the pressure as found in table 3; and the last, the standard enthalpy of vaporization as calculated from equation 3.9.

The pressures obtained for zinc by both the Knudsen effusion and torsion effusion methods do not agree exactly with the values quoted in the literature (Barrow, loc. cit.), but they agree to within 3 percent of each other. They are about 33 percent below the published values.

A least squares Second Law treatment was made with both the Knudsen and torsion pressures. All torsion pressure data obtained prior to point 11 and all Knudsen pressure data obtained prior to 11/12 were omitted as they were unreasonably high. A vapor pressure equation was calculated in the form

$$\log P \text{ (atm.)} = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \quad (3.11)$$

TABLE 3

Vapor Pressure of Zinc, Zinc Run No. 18

Torsion Pressures						Knudsen Pressures							
Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	φ°	P _t (10 ⁻³ Torr)	Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	w (mg.)	t (min.)	P _k (10 ⁻³ Torr)	M
4	290.2	563.4	1.7759	1.51	0.760	4/5	290.1	563.3	1.7762	0.74	60.20	0.701	67
5	290.1	563.3	1.7759	1.57	0.795	5/6	290.0	563.2	1.7756	0.57	46.40	0.700	64
6	290.0	563.2	1.7756	1.57	0.795								
11	289.9	563.1	1.7756	1.24	0.625	11/12	290.2	563.4	1.7759	0.43	40.60	0.604	77
12	290.4	563.6	1.7743	1.23	0.620								
13	287.6	560.8	1.7832	1.07	0.540								
15	289.3	562.5	1.7778	1.11	0.560								
16	299.0	572.2	1.7464	1.85	0.935	16/17	299.4	572.6	1.7464	1.51	88.10	0.986	87
17	299.9	573.1	1.7449	1.94	0.975	17/18	299.1	572.3	1.7473	1.05	64.40	0.937	82
18	298.2	571.4	1.7501	1.80	0.905								
19	308.9	582.1	1.7179	2.95	1.49	19/20	308.7	581.9	1.7185	1.08	47.50	1.32	66
20	308.5	581.7	1.7191	2.92	1.47	20/21	308.3	581.5	1.7197	1.64	66.20	1.44	78
21	308.0	581.2	1.7206	2.89	1.46								
22	315.7	588.9	1.6981	4.02	2.03	22/23	315.6	588.8	1.6984	0.75	23.50	1.86	70
23	315.6	588.8	1.6984	4.00	2.02								
25	315.2	588.4	1.6995	3.96	2.00	25/26	315.0	588.2	1.7001	1.96	59.50	1.92	76
26	314.8	588.0	1.7007	3.92	1.98								
28	325.6	598.8	1.6700	6.36	3.21	28/29	325.4	598.6	1.6706	1.44	28.80	2.94	69
29	325.3	598.5	1.6708	6.34	3.20								
31	324.3	597.5	1.6736	6.29	3.18	31/32	324.6	597.8	1.6728	5.00	98.90	2.97	71
32	324.9	598.1	1.6720	6.37	3.22	32/33	324.9	598.1	1.6720	2.83	54.10	3.07	75
33	324.9	598.1	1.6720	6.38	3.22								
35	333.8	607.0	1.6474	9.29	4.69	35/36	333.6	606.8	1.6480	3.98	53.00	4.45	74
36	333.5	606.7	1.6483	9.21	4.65	36/37	333.5	606.7	1.6483	2.74	36.50	4.44	73
37	333.5	606.7	1.6483	9.31	4.74	37/38	333.7	606.9	1.6477	1.12	15.80	4.20	64
38	333.9	607.1	1.6472	9.34	4.71								

73 ± 5

73 ± 5

torsion constant of the fiber used was 0.163 dyne cm./radian.

TABLE 4

Third Law Calculations of ΔH_{298}° for Zinc

Pt.	t	T	$\frac{G_T^{\circ}(g) - H_{298}^{\circ}(g)}{T}$	$\frac{G_T^{\circ}(c) - H_{298}^{\circ}(c)}{T}$	P	ΔH_{298}°
	($^{\circ}\text{C}$)	($^{\circ}\text{K}$)	(cal/mole deg.)	(cal/mole deg.)	(10^{-3}Torr)	(kcal/mole)

From Torsion Pressures

11	289.9	563.1	-39.273	-10.978	0.625	31.58
12	290.4	563.6	-39.278	-10.986	0.620	31.62
13	287.6	560.8	-39.265	-10.973	0.540	31.63
15	289.3	562.5	-39.272	-10.980	0.560	31.68
16	299.0	572.2	-39.310	-11.030	0.935	31.64
17	299.9	573.1	-39.314	-11.037	0.975	31.62
18	298.2	571.4	-39.309	-11.028	0.905	31.62
19	308.9	582.1	-39.352	-11.085	1.49	31.63
20	308.5	581.7	-39.350	-11.085	1.47	31.62
21	308.0	581.2	-39.347	-11.080	1.46	31.61
22	315.7	588.9	-39.381	-11.142	2.03	31.62
23	315.6	588.8	-39.381	-11.142	2.02	31.63
25	315.2	588.4	-39.378	-11.120	2.00	31.62
26	314.8	588.0	-39.376	-11.116	1.98	31.62
28	325.6	598.8	-39.422	-11.175	3.21	31.61
29	325.3	598.5	-39.420	-11.175	3.20	31.61
31	324.3	597.5	-39.417	-11.167	3.18	31.56
32	324.9	598.1	-39.418	-11.169	3.22	31.58
33	324.9	598.1	-39.418	-11.169	3.22	31.58
35	333.8	607.0	-39.456	-11.219	4.69	31.59
36	333.5	606.7	-39.455	-11.216	4.65	31.58
37	333.5	606.7	-39.455	-11.218	4.74	31.57
38	333.9	607.1	-39.456	-11.217	4.71	31.59
						31.59 $\pm$ 0.05

From Knudsen Pressures

11/12	290.2	563.4	-39.278	-10.986	.604	31.66
16/17	299.4	572.6	-39.314	-11.035	.986	31.62
17/18	299.1	572.3	-39.312	-11.031	.937	31.66
19/20	308.7	581.9	-39.352	-11.085	1.32	31.79
20/21	308.3	581.5	-39.348	-11.083	1.44	31.67
22/23	315.6	588.8	-39.381	-11.142	1.86	31.74
25/26	315.0	588.2	-39.376	-11.126	1.92	31.68
28/29	325.4	598.6	-39.420	-11.175	2.94	31.73
31/32	324.6	597.8	-39.417	-11.167	2.97	31.68
32/33	324.9	598.1	-39.418	-11.169	3.07	31.66
35/36	333.6	606.8	-39.456	-11.219	4.45	31.66
36/37	333.5	606.7	-39.455	-11.216	4.44	31.66
37/38	333.7	606.9	-39.456	-11.218	4.20	31.74
						31.69 $\pm$ 0.05

FIGURE 6 LOG P vs. $1/T$ PLOT FOR ZINC RUN #18.
(INDICES OF POINTS REFER TO TABLE 3)

from which the heat of vaporization ($\Delta H_{\text{vap}}^{\circ}$) for the temperature range considered and the entropy change can be calculated.

The vapor pressure equations, enthalpy, and entropy changes for the vaporization process are tabulated in table 5. The first column contains the type of measurement; the second, the vapor pressure equation; the third, the enthalpy of vaporization; and the last, the entropy of vaporization.

3.4 Discussion

The standard enthalpies of vaporization (ΔH_{298}°) obtained by Third Law calculations are in good agreement with the literature (Barrow, loc. cit.) values, differing by less than 0.5 kcal/mole. The Second Law enthalpies ($\Delta H_{\text{vap}}^{\circ}$) and entropies ($\Delta S_{\text{vap}}^{\circ}$) of vaporization at the temperatures of the experiments are likewise in good agreement, differing also by less than 0.5 kcal/mole and 0.5 cal/mole deg. respectively.

The vapor pressure equations represent pressures which are about 33% below the literature values.

The good agreement between the pressures obtained in this experiment and the close agreement of the enthalpy and entropy of vaporization with the values presented in the literature indicates that the apparatus functions as it was intended.

That the observed pressures are somewhat low may reflect some uncertainty in the temperature calibration, previously acknowledged to be accurate to $\pm 1^{\circ}\text{C}$. It may also reflect some inaccuracy in the measurement of the physical parameters of the torsion cell.

TABLE 5

Vapor Pressure Equations and Thermodynamic Data, Zinc Run #18

Type Measurement	Vapor Pressure Equation	$\Delta H_{\text{vap}}^{\circ}$ (kcal/mole)	$\Delta S_{\text{vap}}^{\circ}$ (cal/mole deg.)
Torsion	$\log P = 5.98 \pm 0.18 - (6.80 \pm 0.10) \times 10^3/T$	31.11 ± 0.48	27.35 ± 0.81
Knudsen	$\log P = 5.87 \pm 0.15 - (6.744 \pm 0.086) \times 10^3/T$	30.86 ± 0.39	26.88 ± 0.67

CHAPTER IV

VAPOR PRESSURE OF BORON SULFIDE

4.1 Introduction to Research on Boron Sulfide

Boron sulfide, B_2S_3 was reported as having been prepared as early as 1819 by J. J. Berzelius²⁹ who burned elemental boron in the vapor of sulfuric acid. In the latter half of the nineteenth century, the compound, as well as metathioboric acid, HBS_2 , was reported as having been prepared by reaction of boron with hydrogen sulfide,³⁰ carbon disulfide,³¹ lead sulfide,³² and by the reaction of hydrogen sulfide with boron trichloride.³³

By 1892 the density of boron sulfide was found to be 1.55, and its melting point was found to be $310^\circ C$.³¹ P. Sabatier³⁴ gave a value of -82.6 kcal/mole as its heat of formation. He further reported that it volatilized in hydrogen at $300^\circ C$.

Several workers, most notably A. Stock,³² reported that metathio-boric acid, prepared by the reaction of dry hydrogen sulfide with boron bromide in benzene or carbon disulfide, could be decomposed to form boron sulfide.

Thermodynamic studies on boron sulfide have been carried out only recently. Greene³⁵ determined the heat of vaporization of boron sulfide by use of its infrared absorption spectra in the range of 640 to $780^\circ C$. and found a value of 36 ± 3 kcal/mole for the heat of vaporization. Later, Greene and Gilles¹ discovered a large number of high molecular weight polymers over samples of sulfur-rich B_2S_3 vaporized in a mass

spectrometer. They obtained a value of 36 ± 5 kcal/mole for the heat of vaporization of B_2S_3 in the range of 360 to 449°C. by use of mass spectrometric intensities. However, neither the infrared absorption spectra studies nor the mass spectrometer studies provided any total pressure data.

4.2 Preparation of Boron Sulfide

The boron sulfide used in these experiments was prepared by the reaction of hydrogen sulfide with elemental boron in vycor tubes. This reaction apparently produces first a mixture of HBS_2 and B_2S_3 which, upon continued heating, decomposes completely to B_2S_3 .³⁶ The reactions would then be:

The apparatus used for the preparation is described in Fig. 7. Technical grade hydrogen sulfide (Matheson Co., Inc., stated to be 98.5% pure) is first purified by washing with a saturated barium hydroxide solution³⁷ so as to remove any polysulfides and carbon and then dried by passing through subsequent calcium sulfate* and magnesium perchlorate columns. The hydrogen sulfide was usually diluted with hydrogen (obtained from the National Gas Company, and stated to be 99.5% pure by the distributor) prior to purification. The hydrogen was added to hinder the decomposition of the H_2S which, if decomposed, would result in the production of free sulfur in the sample.

*The use of $CaSO_4$ as a predrying agent is preferred, however, to $CaCl_2$, as the latter liquifies on the absorption of water and tends to plug² the columns.

FIGURE 7 APPARATUS FOR THE PREPARATION OF B_2S_3 AND HBS_2 .

The dry H_2/H_2S mixture (ratio 2:1) was then passed over a sample of powdered elemental boron (Cooper Metallurgical Associates, Analysis: 99.5% boron, 0.15% iron, and 0.10% carbon, Lot #0764, dated 7-30-64 (B 25)) which was contained in the left end of the first section of the vycor tube. The sample was heated to 500 to 550°C. with a small (6 inch long) resistance furnace for a period of 12 to 24 hours, during which time the product condensed in the cool portion of the first tube section. The furnace was then cooled to 200 to 250°C. and slowly moved along the tube such that the product was transported into the second section of the tube. This process required several days. The H_2/H_2S gas mixture flow was continued during this period. This section was then sealed off and transferred to a dry box where, in order to obtain clean B_2S_3 , the sample was washed with hot benzene to remove any remaining free HBS_2 .* Then samples were taken for analysis, for x-ray powder patterns, and for filling the torsion cell. This cell was subsequently transferred, in air, to the torsion effusion apparatus. The latter process took about ten minutes until the sample was under vacuum, a time sufficiently short such as to minimize the amount of decomposition by atmospheric moisture which would produce boric acid and hydrogen sulfide.

4.3 Analysis

The boron sulfide, obtained by the method described in section 4.2, was analyzed for boron and sulfur. Boron was determined volumetrically in the form of boric acid while sulfur was converted first to sulfate and analyzed gravimetrically as barium sulfate.

*The solubility of HBS_2 in benzene and carbon disulfide is reported by A. Stock.³²

For analysis a sample was divided into two parts, the first for sulfur of 200 mg. and the second for boron of 500 mg.

The sample for sulfur analysis was placed in the Erlenmeyer flask of the apparatus described in Fig. 8. Then 0.01N HCl was slowly added via the dropping funnel. Helium or nitrogen gas was bubbled through the sample at the same time. The evolved H_2S was trapped in 5% ammonical hydrogen peroxide solutions. The decomposition was allowed to continue for twelve or more hours in order to insure that all the H_2S was removed from the sample. The two ammonical peroxide solutions were then combined and boiled to destroy the remaining peroxide and drive off the excess ammonia. The resulting ammonium sulfate solution was neutralized and made slightly acidic by the addition of HCl (2 ml. conc. HCl to 200 ml. solution), and a barium chloride solution was added precipitating barium sulfate. The sulfate was then filtered, washed, ignited, and weighed.⁴⁰

Analysis for boron³⁸ involved allowing the sample to react with water and boiling the resulting solution to drive off the evolved H_2S . The resulting boric acid solution was diluted with CO_2 -free water in a volumetric flask to 250 ml. and 25 ml. aliquots were taken for analysis.³⁹ The aliquots were transferred to a 600 ml. beaker and diluted to 250 ml. with CO_2 -free water. Forty grams of mannitol were added, and the sample titrated to a pH of 6.30 with 0.1N NaOH with a pH meter. Normally the starting pH must be adjusted to a value of 6.30 prior to the addition of the mannitol, but in the case of these analyses, the starting pH was already of that value.

Results of the analysis for the sample used in these experiments

FIGURE 8 APPARATUS FOR SULFUR ANALYSIS

were as follows:

TABLE 6
Analysis of Boron Sulfide

Element	Found (%)	Expected for B_2S_3 (%)	Expected for HBS_2 (%)
Sulfur	78.7 ± 0.2	81.64	84.44
Boron	17.87 ± 0.01	18.36	14.24
Total	96.6 ± 0.2		

The sum of the boron and sulfur values obtained is less than 100%. However, the ratio of sulfur to boron is more nearly that as in B_2S_3 than that in HBS_2 . Hence, it was concluded that the material was primarily B_2S_3 . No free sulfur was present since no turbidity, indicating the presence of free sulfur, was observed in the aqueous solutions of the sample. The remaining 4% probably consisted of oxygen, introduced by hydrolysis, and possibly silicon, introduced from the vycor reaction tubes.

4.4 Vapor Pressure, Experimental

A sample of boron sulfide, prepared and analyzed as described in sections 4.2 and 4.3 and weighing 184 mg. was vaporized in the vacuum-balance-torsion-effusion apparatus. The torsion crucible plus sample weighed 10.170 g. in air.

The crucible was placed in the apparatus following the procedure

as described in section 2.4. It was heated rapidly to 150°C . during which it lost 2 mg., after which it was slowly heated over a period of two weeks to 500°C . During this period about 5% of the sample vaporized, although at a low rate, less than 0.1 mg. per hour. The sample was heated for 12 to 15 hours each day, and the furnace was turned off each night. No change was ever observed in the sample due to cooling and the pressure of the previous heating could always be reestablished upon reheating. At 500°C . the first measurable torsion pressure was obtained. The temperature was increased stepwise, with both weight loss and torsion measurements being taken at each step. At 540°C . the pressure began to drop although the temperature remained relatively constant. After a few hours, the pressure again became constant and the stepwise temperature increase continued to 550°C . The sample was cooled overnight, and at the next heating the temperature was increased stepwise to 592°C . At this time the deflection of the torsion apparatus was so great that it could no longer be read. The temperature was then lowered stepwise, and measurements were taken. The sample was allowed to cool to room temperature and at the next heating experiment was heated only to 520°C . The temperature was then increased slowly to 560°C . after which the pressure began to drop although the temperature was constant. The temperature was further increased, with intermittent nightly cooling, although the pressure continued to drop. The temperature reached a maximum value of 603°C ., and the sample was reduced to about 7% of its original mass. After this, the weight loss rate became very slow, less than 0.05 mg. per hour. The crucible weighed 10.002 g. after removal from the apparatus.

No temperature calibration had been made in the 300 to 600°C .

range for it was not anticipated that this range would be encountered. Therefore, the temperature correction values from the 100 to 300°C. calibration were extrapolated, based upon the assumption that the temperature difference between the reference and the torsion cell were becoming constant, thereby yielding a constant correction of 46°C. This correction was added to all the reference temperatures obtained in the 500 to 600°C. range in order to obtain a more accurate temperature.

4.5 Vapor Pressure, Results

The torsion pressures obtained in these experiments are shown in tabulated form in table 7, and as a log P versus 1/T plot of the torsion pressure in Fig. 9. The first column in table 7 contains the identification number of the measurement; the second, the temperature in degrees centigrade; the third, the absolute temperature; the fourth, the reciprocal of the absolute temperature; the fifth, the angular displacement; and the last, the torsion pressure as calculated using equation 1.24.

The weight loss values are shown in table 8. The first column contains the set number; the second, identification of the reference period; the third, the temperature in degrees centigrade; the fourth, the absolute temperature; the fifth, the reciprocal of the absolute temperature; the sixth, the mass loss during the reference period; the seventh, the duration of the reference period; the eighth, the rate of weight loss; the ninth, the average torsion pressure during the reference period; the tenth, the molecular weight of the vapor calculated from the average torsion pressure, as calculated using

equation 1.26, the temperature, and the weight loss rate; and the last, the average of the molecular weights for each set of data.

The weight loss data have been used to calculate Knudsen Pressures, assuming the molecular weight to be that of boron sulfide ($M = 117.84$). The Knudsen effusion equation for crucible #2 is therefore:

$$P_k(\text{Torr}) = 19.43(w/t)(T/M)^{\frac{1}{2}} \quad (4.3)$$

where w/t is in grams per minute. These pressures, designated as P_E are tabulated in table 9 and are represented as a $\log P_E$ versus $1/T$ plot in figure 10. The first column in table 9 contains the identification of the measurement period; the second, the temperature in degrees centigrade; the third, the absolute temperature; the fourth, the reciprocal of the absolute temperature; the fifth, the weight loss rate; the sixth, the product of the weight loss rate and the square root of the absolute temperature; and the last, the Knudsen pressure as calculated using equation 4.3 and the molecular weight of boron sulfide.

The data seem to fall into three distinct linear $\log P$ to $1/T$ relationships, which are called for purposes of convenience sets one, two, and three.

For each set of data a least squares treatment was made, using the procedure described in section 3.3 and the resulting vapor pressure equations, enthalpy, and entropy of vaporization are tabulated in table 10. The first column of this table contains the set number; the second, the temperature range considered; the third gives the type of measurement made, either torsion or Knudsen; the fourth, the vapor pressure equation; the fifth, the enthalpy of vaporization; and the last, the entropy of vaporization.

TABLE 7

Torsion Pressures, Boron Sulfide Run #1

Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	φ°	P _t (10 ⁻³ Torr)
67	513.8	787.0	1.2710	0.60	0.300
68	512.6	785.8	1.2716	0.58	0.290
69	523.4	796.6	1.2553	1.04	0.525
70	523.2	796.4	1.2557	1.02	0.515
71	530.2	803.6	1.2444	1.49	0.750
72	530.2	803.6	1.2444	1.43	0.720
75	549.4	822.6	1.2157	2.88	1.45
76	546.2	819.4	1.2204	2.51	1.27
77	545.2	818.4	1.2219	2.40	1.21
78	543.0	816.2	1.2252	2.12	1.07
79	543.0	816.2	1.2252	2.07	1.05
80	543.0	816.2	1.2252	2.01	1.02
81	546.8	820.0	1.2195	2.69	1.36
82	548.2	821.2	1.2177	2.37	1.20
86	559.2	832.4	1.2013	2.68	1.35
87	557.2	830.4	1.2042	2.43	1.23
88	556.4	829.6	1.2054	2.34	1.18
89	566.5	839.7	1.1909	3.75	1.90
90	566.2	839.4	1.1913	3.66	1.85
91	576.2	849.4	1.1773	6.02	3.04
92	576.2	849.4	1.1773	6.18	3.12
93	576.3	849.6	1.1770	5.79	2.98
95	585.5	858.7	1.1646	10.39	5.25
96	585.5	858.7	1.1646	10.34	5.20
97	591.4	864.6	1.1566	13.37	6.75
98	591.2	864.4	1.1568	13.74	6.70
99	588.4	861.6	1.1606	11.79	5.95
101	588.6	861.8	1.1604	11.82	5.96
102	588.4	861.6	1.1606	11.74	5.95
104	584.2	857.2	1.1666	9.52	4.80
105	584.2	857.2	1.1666	9.52	4.80
108	523.8	797.0	1.2547	0.49	0.250
109	520.8	794.0	1.2594	0.42	0.210
110	522.2	795.4	1.2572	0.44	0.222

TABLE 7, Continued

Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	ϕ°	P _t (10 ⁻³ Torr)
111	522.4	795.6	1.2570	0.46	0.233
112	527.5	800.7	1.2489	0.58	0.291
113	526.8	800.0	1.2500	0.57	0.285
114	537.6	810.8	1.2333	0.96	0.483
115	537.0	810.2	1.2343	0.94	0.475
117	543.0	816.2	1.2252	1.23	0.620
118	556.2	829.4	1.2057	2.24	1.13
119	555.0	828.2	1.2074	2.14	1.08
120	562.6	835.8	1.1964	3.00	1.51
121	562.4	835.6	1.1968	2.99	1.51
123	568.4	841.6	1.1882	3.89	1.97
127	570.8	844.0	1.1848	4.18	2.11
130	574.5	847.7	1.1797	4.69	2.37

FIGURE 9 BORON SULFIDE RUN No. 1 PLOT OF TORSION PRESSURES
(INDICES OF POINTS REFER TO TABLE 7)

TABLE 8

Weight Loss Values, Boron Sulfide Run No.1

Set	Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	w (mg.)	t (min.)	w/t (10 ⁻⁶ g./min.)	P _t (10 ⁻³ Torr)	M	M _{avg.}
1	62/64	504.9	778.1	1.2853	0.41	118.00	3.47	0.187	102	
	67/68	513.2	786.4	1.2720	0.57	101.20	5.63	0.295	108	
	69/70	523.3	796.5	1.2553	0.36	39.30	9.16	0.520	93	
	71/72	530.2	803.4	1.2444	2.41	178.70	13.50	0.735	102	101 ± 8
2	86/87	558.2	831.4	1.2028	1.06	45.80	23.14	1.29	101	
	87/88	556.8	830.0	1.2048	0.80	36.80	21.74	1.20	103	
	89/90	566.4	839.6	1.1910	2.18	65.30	33.38	1.87	101	
	91/92	576.2	849.4	1.1773	2.96	54.00	54.81	3.08	102	
	92/93	576.3	849.5	1.1773	3.71	65.90	56.30	3.05	109	
	95/96	585.5	858.7	1.1646	3.02	31.90	94.67	5.22	107	
	97/98	591.3	864.5	1.1567	4.12	34.50	119.4	6.72	103	
	101/102	588.5	861.7	1.1605	4.57	42.60	107.3	5.96	105	
	104/105	584.2	857.4	1.1666	4.09	47.60	85.92	4.80	104	104 ± 3
3	110/111	522.3	795.5	1.2571	0.27	58.40	4.623	0.228	125	
	112/113	527.2	800.4	1.2494	0.26	47.80	5.649	0.288	116	
	114/115	537.3	810.6	1.2337	0.52	56.00	9.286	0.479	115	
	116/117	543.0	816.2	1.2252	0.48	39.70	12.09	0.620	117	
	118/119	556.6	828.8	1.2074	2.76	130.50	21.15	1.11	114	
	120/121	562.5	835.7	1.1966	0.96	34.80	27.59	1.51	105	
	121/122	562.4	835.6	1.1968	0.85	31.30	27.16	1.51	102	113 ± 10

TABLE 9

Knudsen Pressures, Boron Sulfide Run #1

Pt.	t (°C.)	T (°K.)	1/T (10 ⁻³ °K ⁻¹)	w/t (10 ⁻⁶ g./min.)	(w/t)T ^{$\frac{1}{2}$} (*)	P _E (10 ⁻³ Torr)
62/64	504.9	778.1	1.2853	3.47	0.9678	0.173
67/68	513.2	786.4	1.2720	5.63	1.579	0.283
69/70	523.3	796.5	1.2553	9.16	2.585	0.463
71/72	530.2	803.6	1.2444	13.50	3.826	0.684
86/87	558.2	831.4	1.2028	23.14	6.544	1.17
87/88	556.8	830.0	1.2048	21.74	6.263	1.12
89/90	566.4	839.6	1.1910	33.38	9.670	1.73
91/92	576.2	849.4	1.1773	54.81	15.97	2.86
92/93	576.3	849.5	1.1773	56.30	16.41	2.94
95/96	585.5	858.7	1.1646	94.67	27.74	4.96
97/98	591.3	864.5	1.1567	119.4	35.10	6.28
101/102	588.5	861.7	1.1605	107.3	31.68	5.67
104/105	584.2	857.4	1.1666	85.92	25.30	4.53
110/111	522.3	795.5	1.2571	4.623	1.304	0.233
112/113	527.2	800.4	1.2494	5.649	1.598	0.286
114/115	537.3	810.6	1.2337	9.286	2.644	0.473
116/117	543.0	816.2	1.2252	12.09	3.454	0.618
118/119	555.6	828.8	1.2074	21.15	6.089	1.09
120/121	562.5	835.7	1.1966	27.59	7.976	1.43
121/122	562.4	835.6	1.1968	27.16	7.852	1.41

*units are 10⁻⁴ g. deg. ^{$\frac{1}{2}$} /min. See table 2 for cell parameters.

FIGURE 10 PLOT OF KNUDSEN PRESSURES, BORON SULFIDE RUN NO. 1.
(INDICIES OF POINTS REFER TO TABLE 9)

TABLE 10

Vapor Pressure Equations and Thermodynamic Values, Boron Sulfide Run #1

Set	Temp. Range (°C.)	Type Measurement	Vapor Pressure Equation (Atmospheres)	$\Delta H_{\text{vap}}^{\circ}$ (kcal/mole)	$\Delta S_{\text{vap}}^{\circ}$ (cal/deg. mole)
1	512 to 530	Torsion	$\log P = 12.38 \pm 0.39 - (1.477 \pm 0.031) \times 10^4/T$	67.6 ± 1.4	56.6 ± 1.8
		Knudsen	$\log P = 12.04 \pm 0.30 - (1.454 \pm 0.023) \times 10^4/T$	66.5 ± 1.1	55.1 ± 1.4
2	556 to 591	Torsion	$\log P = 13.62 \pm 0.27 - (1.614 \pm 0.023) \times 10^4/T$	73.9 ± 1.1	62.3 ± 1.3
		Knudsen	$\log P = 13.4 \pm 1.2 - (1.600 \pm 0.099) \times 10^4/T$	73.2 ± 4.5	61.4 ± 5.3
3	520 to 575	Torsion	$\log P = 10.06 \pm 0.26 - (1.319 \pm 0.021) \times 10^4/T$	60.36 ± 0.98	46.1 ± 1.2
		Knudsen	$\log P = 9.97 \pm 0.11 - (1.312 \pm 0.087) \times 10^4/T$	60.01 ± 0.40	45.63 ± 0.49

In order to observe any changes in the sample during the vaporization process, a plot was made containing the percentage sample vaporized, the temperature, the pressure and the weight loss rate, all as a function of time. This plot, called the Vaporization Profile, is shown in Fig. 11, and the data are tabulated in table 11. The first column contains the identification of the measurement; the second, the elapsed time during which the sample was heated; the third, the percentage of sample vaporized; the fourth, the weight loss rate for the period covered during the elapsed time period; the fifth, the torsion pressure as calculated from equation 1.24; and the last, the temperature.

The breaks in the tabulation of the data indicate those times when the sample was cooled. These cooling points are also indicated in the plot (Fig. 11) by breaks in the temperature curve.

This plot indicates that both the torsion pressure and the weight loss rate bear approximately the same relationship to the temperature, independent of the amount of sample remaining. Changes in temperature produced corresponding changes in pressure and weight loss rate except after 70% of the sample had been vaporized, where after they dropped off rapidly even though the temperature was increased to 600°C. The sample continued to lose mass at a measurable rate until 93% had been vaporized, at which point the weight loss rate had become very slow, less than 0.05 mg. per hour.

4.6 Discussion

The results of the experiment establishes the usefulness of the apparatus to study the boron sulfide system and provides some insight into the vaporization process.

TABLE 11

Vaporization Profile, Boron Sulfide Run #1

Pt.	elapsed time (hour)	m/m ₀ (%)	w/t (10 ⁻⁶ g./min.)(10 ⁻³ Torr)	P _t	t (°C.)
1	0	x	x	<10 ⁻⁴	<200
2	2	x	x	"	"
3	3	x	x	"	"
4	4	x	x	"	"
5	4.5	x	x	"	"
6	5	x	x	"	"
7	6	1.7	x	"	"
8	12	1.9	x	"	"
9	21	1.9	x	"	"
12	22	2.0	x	"	"
13	23	2.0	x	"	"
14	24	2.1	1.22	"	"
15	26	2.1	1.76	"	"
16	26.5	2.1	1.34	"	208.4
17	27	2.2	1.28	"	226.2
18	29	2.2	0.90	"	224.9
19	30	2.3	x	"	240.8
20	32	2.4	x	"	243.1
21	33	2.4	x	"	242.6
22	34	x	x	"	x
23	35	x	x	"	x
25	36	2.6	x	"	x
26	37	x	x	"	284.0
27	38.5	x	x	"	x
28	40	x	x	"	x
29	41	x	x	"	x
30	43	x	x	"	x
31	44	2.6	x	"	317.8
32	45	2.7	1.67	"	317.4
33	46	2.7	x	"	x
34	47	2.8	x	"	x
35	59	x	x	"	x
36	60	x	x	"	x
37	62	3.4	1.8	"	335.0
38	63	3.5	1.6	"	334.1
39	64	3.5	1.1	"	334.4
40	65	x	3.3	"	x

TABLE 11, Continued

Pt.	elapsed time (hour)	m/m ₀ (%)	w/t (10 ⁻⁶ g./min.)	P _t (10 ⁻³ Torr)	t (°C.)
41	66	3.7	3.6	< 10 ⁻⁴	342.3
42	67	3.9	2.1	"	342.4
43	68	x	3.2	"	x
44	68.5	x	x	"	x
45	69	x	x	"	x
46	71	x	x	"	x
47	72	x	x	"	x
48	73	x	x	"	x
49	75	4.3	0.9	"	373.2
50	76	4.4	0.7	"	372.5
51	77	4.4	1.3	"	372.3
52	81	4.5	2.8	"	401.8
53	82	4.7	1.8	"	400.4
55	82.5	x	x	"	x
56	83	x	1.1	"	x
57	84	x	0.4	"	x
58	85	4.8	1.3	"	451.5
59	87	4.9	0.6	"	451.0
60	88	4.9	1.1	"	469.0
61	90	5.0	8.4	"	471.2
62	91	5.1	3.7	"	505.2
63	92	5.2	3.7	"	504.8
64	93	5.3	3.5	"	504.6
66	94	x	3.2	x	x
67	95.5	5.9	x	0.300	513.8
68	97	6.2	5.6	0.290	512.6
69	98	6.8	x	0.525	523.4
70	99	6.8	9.2	0.530	523.2
71	100	7.3	13.7	0.750	530.2
72	103	8.7	14.0	0.720	530.2
74	104	x	x	x	x
75	104.5	x	29.1	1.45	549.4
76	105	10.5	24.6	1.27	545.2
77	105.5	10.8	23.5	1.21	543.0
78	107	11.7	20.5	1.07	543.0
79	108	12.2	19.0	1.05	543.0
80	109	13.0	18.9	1.02	546.8
81	110	13.3	21.0	1.36	548.2
82	111	14.5	22.0	1.20	548.2
84	112	x	x	x	x

TABLE 11, Continued

Pt.	elapsed time (hour)	m/m ₀ (%)	w/t (10 ⁻⁶ g./min.)	P _t (10 ⁻³ Torr)	t (°C.)
85	112.5	x	30.5	x	x
86	113	17.0	25.8	1.35	559.2
87	114	17.6	29.9	1.23	557.2
88	114.6	18.0	21.7	1.18	556.2
89	115	19.4	33.1	1.90	556.5
90	116	20.6	33.5	1.85	566.2
91	117	22.2	50.9	3.04	576.2
92	118	23.8	54.6	3.12	576.2
93	119	25.8	56.0	2.79	576.3
94	120.5	x	x	x	x
95	121.5	31.9	92.8	5.25	585.5
96	122	34.5	94.7	5.20	585.5
97	122.3	34.6	108.4	6.75	591.4
98	123	36.9	119.4	6.70	591.2
99	123.5	39.3	112.1	5.95	588.4
100	124	x	x	x	x
101	124	40.6	105.9	5.95	588.6
102	125	43.1	107.3	5.95	588.4
103	126	x	90.8	x	x
104	127	46.1	85.6	4.80	584.2
105	128	48.3	85.9	4.80	584.2
107	129	x	x	x	x
108	130	49.4	5.5	0.250	523.8
109	130.5	49.5	x	0.210	520.8
110	131	49.5	3.4	0.222	522.2
111	132	49.6	4.6	0.233	522.4
112	132.6	49.8	5.6	0.291	527.5
113	133.6	49.9	5.7	0.285	526.8
114	134	50.0	8.7	0.483	537.6
115	135	50.3	9.3	0.475	537.0
116	135.2	50.4	10.2	x	x
117	136	50.6	12.1	0.620	543.0
118	136.3	50.8	19.5	1.13	556.2
119	138.3	52.3	21.2	1.08	555.0
120	138.6	52.7	26.1	1.51	562.6
121	139	53.2	27.6	1.51	566.4
122	139.5	53.7	27.2	1.97	568.4
123	140	54.1	33.8	2.11	570.8
124	141	54.9	34.7	2.37	574.5
125	142	56.0	32.5	x	567.8
126	143	58.6	x	2.41	573.4
127	144	59.4	x	2.11	570.8

TABLE 11, Continued

Pt.	elapsed time (hour)	m/m ₀ (%)	w/t (10 ⁻⁶ g./min.)	P _t (10 ⁻³ Torr)	t (°C.)
128	144.5	60.2	31.7	1.98	569.2
129	146.5	63.5	34.2	1.81	568.0
130	147.3	64.4	40.8	2.37	574.5
131	148.3	65.8	43.2	2.30	574.2
132	149.3	67.2	48.3	2.73	578.0
133	151	69.5	48.8	2.66	578.0
134	152	71.7	x	3.37	589.5
135	152.5	72.7	59.9	3.36	584.8
136	153	73.6	51.2	2.72	582.0
137	153.6	74.8	56.7	3.22	586.5
138	154.5	76.1	53.2	2.90	585.5
139	156	78.5	48.1	2.53	585.2
140	157	80.0	47.6	2.30	585.2
141	158	81.2	38.8	2.05	585.2
142	159.5	82.8	33.8	1.83	585.0
143	163.5	85.8	25.9	1.12	585.2
144	165	86.8	17.1	0.883	585.0
145	169	89.3	14.2	0.485	587.2
146	170	89.3	14.9	0.762	605.2
147	171	89.8	11.9	0.578	604.2
148	173	90.4	8.7	0.388	604.2
149	175	90.8	6.2	0.283	604.2
150	177	91.1	5.9	0.152	604.0
151	179	91.5	3.6	0.156	603.6
152	191	92.2	1.7	0.0455	603.0
153	193	92.3	1.2	x	603.0
154	198	92.6	1.1	x	603.7
156	201	92.8	0.9	x	603
157	205	92.9	x	x	603
158	207	92.9	x	x	603

FIGURE 11 VAPORIZATION PROFILE, BORON SULFIDE RUN NO. 1 .
 (—●— = % SAMPLE REMAINING, —●— = TEMPERATURE, - - ○ - - = $\log(w/t)$, AND - · - · = $\log P$)

The most notable observation is the changing vaporization pattern indicated by the breaks in the pressure to temperature relationships. These appear as three distinct sets. These may well represent three distinct processes. These changes support the observations of Greene and Gilles¹ at this laboratory. Their studies on sulfur-rich samples of boron sulfide indicated the presence of a large number of substances in the vapor phase, and that the proportions of these substances changed with time. The sample used in this experiment differed significantly from the one used in their studies, for this sample contained no free sulfur.

The plot of the vaporization profile, as shown in Fig. 11, indicates that the sample did not change appreciably during the vaporization since pressures could be reproduced by identical temperatures at various times during the experiment, except after 70% of the sample had been vaporized.

The enthalpy and entropies, as calculated from the slopes of the plots and the pressure equations (Table 7), respectively, are of uncertain accuracy due to a lack of accurate thermocouple calibration. A ten degree error in either end of the temperature range studied would produce an entropy and enthalpy difference of ten kcal/mole and twelve kcal/mole deg., respectively.

The precision between the experimental observations is very good and can be considered as significant. This suggests the existence of at least three separate vaporization processes.

The impossibly high entropy values make it unreasonable to assume that the enthalpies are correct; hence, no reliable thermodynamic data can be derived from this experiment.

CHAPTER V

SUGGESTIONS FOR FUTURE RESEARCH

The experiments carried out indicate the applicability of this instrument for the study of boron sulfide. The results suggest several experiments which might provide more information about this system.

The most obvious starting point would be to establish a more accurate temperature calibration, particularly in the 300 to 600°C. range. This would be necessary for all future experiments and could be used to correct and evaluate more fully the results already obtained.

Since the vapor composition appeared to change with time, it would be desirable to measure the pressure, and hence, molecular weight, at a constant temperature over extended periods of time. The results would indicate whether any impurities in the sample were vaporizing simultaneously as their pressure contribution would be expected to drop off more rapidly with time.

Instead of studying boron sulfide directly, it might be of greater value to start with metathioboric acid, HBS_2 , and decompose this material in the torsion cell by heating. By using this procedure, the sample could be observed as its composition approaches B_2S_3 from HBS_2 . This would remove the uncertainty introduced by using samples of B_2S_3 contaminated with small amounts of HBS_2 .

The addition of sulfur to boron sulfide samples which contain no free sulfur could be utilized to give some indication of the pressure

dependence of the sample upon the sulfur activity.

This instrument is applicable not only to the study of vapor pressures above boron sulfide but can also be utilized with any materials having vapor pressures in the 10^{-5} to 10^{-2} Torr at temperatures up to 1100°C .

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