A STUDY OF THE SILICON BORON PHASES AND A DETERMINATION OF THE ENTHALPY OF VAPORIZATION AND FORMATION OF SILICON HEXABORIDE

by

Warren A. Knarr
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Advisory Committee:

Redacted Signature

Chairman

Redacted Signature

Redacted Signature

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I PURPOSE OF RESEARCH

As a result of the problems associated with atomic energy and rocket programs, there is an interest in finding and studying compounds which can withstand temperatures in excess of 1000°C. without undergoing phase changes, dissociation, or reaction with other compounds. Reliable predictions of high temperature behavior can be made only if the thermodynamic properties and phase relationships of the compound are known or can be estimated accurately.

The refractory natures of boron carbide and silicon carbide have enabled them to be used for many purposes at high temperatures. From the positions of silicon, boron, and carbon in the periodic table, it was reasoned that silicon and boron might form one or more compounds and that possibly one of these compounds might have properties which would make it desirable for use at high temperatures.

When research for this thesis was started in August 1957, a literature search revealed that recent workers were unable to find any intermediate phases in the silicon boron system even though the preparation of SiB_3 and SiB_6 was reported around the turn of the century. Since the recent studies did not appear to be exhaustive, it seemed desirable to determine whether compounds existed in the silicon boron system, and, if so, measure some of their thermodynamic properties and phase relationships.

After research was started in this laboratory reports of compound formation appeared. Unsuccessful attempts to duplicate in this laboratory many of the reported compounds gave rise to the suspicion that many of the reports were in error.

The research consisted of four parts, the preparation and characterization of the solid phases in the silicon boron system, the establishment of the temperature-composition phase diagram, the establishment of the pressure-composition phase diagram, and the determination of the enthalpy and entropy of vaporization and formation of the compounds which were found to have a vapor pressure which could be measured by available methods.

High temperature and high vacuum techniques, X-ray diffraction studies, vapor pressure measurements, chemical analyses, and the search for and choice of suitable substances and their fabrication into crucibles were all involved in this research. Vaporization studies have proved to be an effective way to obtain thermodynamic information.

II RELATED LITERATURE

This section contains abstracts of pertinent literature references appearing both before and after research was initiated. The reliability of the work reported in the references will be discussed after the experimental results have been presented.

The initial preparation of compounds between silicon and boron was reported by Moissan and Stock (1) in 1900. They indicated that SiB_3 and SiB_6 could be formed by melting five atomic parts of silicon with one atomic part of boron in an electric arc. They stated that the resulting mixture was from 10 to 20% SiB_3 and 80 to 90% SiB_6. The two compounds were separated from each other by selective treatment with HNO_3 and KOH. It was reported that KOH destroyed preferentially the SiB_3 whereas the HNO_3 preferentially destroyed the SiB_6. Watts (2) was unable to duplicate the work of Moissan and Stock. However, in both cases the resulting material was repeatedly treated with caustic agents to try to attain a constant ratio between the two elements. This constant ratio was the criterion of the attainment of a compound.

Brewer, Sawyer, Templeton, and Dauben (3) heated two different ratios of silicon to boron. They heated one sample containing 50 at. percent boron and on another occasion a sample was heated containing 80 at. percent boron in a BeO crucible for 20 minutes at 1725°C. From their X-ray diffraction patterns they identified silicon and found a few weak lines which they attributed to boron. Stavrolakis, Barr, and Rice (4) cold pressed mixtures of silicon and boron in 1:1 and 1:4 atomic ratios and then heated them to temperatures of 1400°C. They could identify only silicon from the X-ray diffraction patterns.

After experimental investigations for this thesis were started, there appeared reports which indicated the pre-existence of SiB_3. The first was that of Samsonov and Latysheva (5) who reported the preparation of SiB_3. They stated that the compound was obtained by hot compression of mixtures of silicon and boron. They also said that the compound could be formed by the reduction of B_2O_3 and SiO_2 with magnesium. They reported a tetragonal unit cell for SiB_3 with $a_o = 2.829 \pm 0.007$ and $c_o = 4.765 \pm 0.013$ Å; however, they gave no indication of the space group nor did they report any intensity measurements. Gurevich, Epel'baum and Ormont (6) have questioned the structure determination of Samsonov and Latysheva, but as yet no reference has been found in which Samsonov and Latysheva replied to the criticism.

Rizzo (7) has stated that he also has obtained a phase which he believes to be SiB_3 or SiB_4. From single crystal X-ray diffraction patterns of the material he has determined that it has a hexagonal unit cell with the parameters $a_o = 5.52$ and $c_o = 12.70$ Å. He obtained his material from a melt of the solution of silicon in B_2O_3. Finally, reports (7) indicate that Cline has single crystals which he believes to be either SiB_3 or SiB_4. The X-ray diffraction patterns of Cline's crystals enable him to calculate a hexagonal unit cell with $a_o = 3.10$ and $c_o = 12.55$ Å.

Several journal articles which indicated the preparation of SiB_6 appeared after research was begun; however, as with SiB_3 the reports appear too conflicting. A paper by Samsonov and Markovski (8) describes the preparation of SiB_6 which was supplied to Zhuravlev (9) who decided that the material was isomorphic with CaB_6. He indicated $a_o = 4.150 \pm 0.002$ Å for the parameter of the cubic unit cell of SiB_6. The accepted value for CaB_6 is $a_o = 4.153$ Å.

After this research was started, papers by Cline (10, 11) appeared in which he reported the preparation of SiB_6 by heating a mixture of boron and an excess of silicon. The compound obtained was found to have an orthorhombic unit cell with the lattice parameters $a_o = 14.392 \pm 0.0010$, $b_o = 18.267 \pm 0.0015$, and $c_o = 9.885 \pm 0.0010$ Å. The above measurements were made from Weissenberg photographs taken about the b and c axes. Adamsky (12) continued the work of Cline and indicated that the probable space group for this form of SiB_6 was Pnn2 or Pnnm. In addition, he postulated that the arrangement of the atoms resembled that of B_4C reported by Clark and Hoard (13) in that groups of twelve boron atoms are arranged at the vertices of an icosahedron. Groups of two silicon atoms take the place of the linear chains of three carbon atoms which are present in B_4C. Adamsky and Cline were unable to find any evidence of a cubic SiB_6. Cline indicated the melting point of SiB_6 to be 1950°C.

Not only have reports appeared recently to support the existence of SiB_3 and SiB_6, but in addition the existence of another compound, SiB_{12}, has been proposed by Parthe (14). He prepared it by heating boron and silicon in a BN crucible at 2200°C. The products obtained from the heating were identified by him as silicon and SiB_{12}. He reported a melting point for the SiB_{12} of approximately 2200°C. He found that the material had an orthorhombic unit cell with $a_o = 11.10$, $b_o = 14.79$, and $c_o = 10.12$ Å.

The above compound reported by Parthe may or may not have been the compound referred to by Powell (15). He listed the reduction at a heated surface by hydrogen of $SiCl_4$ and BCl_3 as a method for the preparation of a compound which he identified as SiB_n. Nowotny, Dimakopoulou, and Kudielka (16) were aware of Powell's work and indicated that n would have a value equal to or greater than ten on the basis of their own work.

The last authors also presented evidence for the solubility of boron in solid silicon. Their evidence was in the form of a shift in the lattice parameters from 5.430 for the pure silicon as given by Straumanis and Akc (17) to 5.384 Å for the silicon phase in equilibrium with a phase more rich in boron.

III METHODS OF APPROACH

In this section a description will be given of the various methods which were used to confirm and to search for new solid phases of the silicon boron system, to establish the condensed state phase diagram, to study the vaporization characteristics of the various phases, and to calculate the enthalpy and entropy of the vaporization and formation of compounds. The identification of compounds and the establishment of the condensed state phase diagram are interrelated problems, therefore a separate discussion of the methods of approach for this phase of the research will not be given.

A. Identification of Compounds and the Establishment of the Temperature-Composition Phase Diagram

When one is concerned with a high temperature condensed system, one finds it is convenient to consider a compound as a phase with a limited range of homogeneity. If a particular phase has a limited homogeneity range and in addition the composition of the phase is a simple ratio of the components, the phase is frequently referred to as a compound.

The establishment of the phase diagram was based on the phase law. The phase law,

$$F = C - P + 2 \tag{1}$$

gives the number of degrees of freedom, F, as a function of the number of components in the system, C, and the number of phases present, P. Since the syntheses used to establish the temperature-composition diagram for the two component system, silicon and boron, were carried out under conditions which permitted the establishment of a vapor phase; the maximum number of condensed phases which could exist over a range of temperatures was two.

Syntheses which resulted from heating various ratios of silicon and boron were examined by means of X-ray diffraction to determine which diffraction lines were associated with which compositions. The presence of a two phase region could be detected by preparing a group of syntheses of gradual changing composition. If all of the syntheses were within the two phase region, the X-ray diffraction patterns would show one group of lines decreasing in intensity and one group increasing in intensity as the composition changed. If the same procedure were used and the position of the lines with respect to one another changed, it was concluded that the syntheses of this group represented a single phase region.

If one were to pass from a two phase region to a one phase region, it follows that one group of lines would disappear. If one were to pass from a two phase region, through a region of limited homogeneity, and then into a second two phase region; it is apparent that one group of lines would disappear and another group would appear. The diffraction lines which appeared on both sides of the region of limited homogeneity would be those of the region of limited homogeneity. This was the method used to establish which diffraction lines were associated with a compound.

It is apparent that different phases might exist at different temperatures. It was necessary to make heatings at many temperatures and to quench the samples in order to determine the phase changes which resulted from the variation of the temperature.

The attainment of equilibrium between solid phases was measured in two ways. If the phases of a synthesis changed as a result of additional heating at the same temperature, equilibrium was assumed not to have been attained as a result of the initial heating. If after heating a sample at an arbitrary temperature three condensed phases remained in violation of the phase rule and two of the phases were the phases present before the heating was initiated, it was assumed that the sample had been heated insufficiently to establish equilibrium.

B. Determination of Pressure-Composition Diagrams

Before considering the methods used to determine the pressure-composition diagrams for the silicon boron system one must consider the possible modes of vaporization.

Gilles (18) has already presented a treatment of the subject, but a summary is desirable.

The various vaporization processes may readily be divided into two categories, congruent and incongruent. In the case of the congruent process the overall vapor composition does not differ from that of the phase which is the source of the vapor. In such a system the continued vaporization of the material does not cause a change to occur in the composition of the condensed phase. In the case of the incongruent process the overall vapor composition is different from that of the condensed phase from which it originated. Continued vaporization does result in a change in the composition of the condensed phase which vaporized incongruently.

In the case of the congruent vaporization, the vapor need not be composed of the same molecules which are found in the condensed phase. The vapor may consist of dissociated molecules or new molecules. The only requirement is that the overall stoichiometry of the vapor must be equal to that of the condensed phase. Thus, if SiB_6 were to vaporize congruently the vapor might consist of SiB_6 molecules, silicon and boron atoms in the ratio of one to six, or one SiB_4 molecule might be present for each SiB_8 molecule.

For the incongruent vaporization process the condensed phase may vaporize one of the components preferentially, may vaporize a molecule of different stoichiometery and give rise to one of the components in the condensed phase, or finally the condensed phase may produce a vapor and condensed phase which consist of molecules of composition different from that of the initial condensed phase.

If SiB_6 were to vaporize incongruently it might preferentially vaporize silicon and form a condensed phase more rich in boron, or a vapor such as SiB_3 and solid boron might result from the vaporization of SiB_6, or instead of solid boron, there might be a new condensed phase richer in boron. The above are only illustrative examples and by no means do they include all of the possibilities.

The phase rule will now be referred to again, since it is useful in predicting whether the vapor pressure of a system will only be a function of the temperature or whether it will be a function of the temperature and the composition. The question to be answered by the phase rule in this discussion is how many variables must be fixed in order to fix the vapor pressure.

If one has a congruently vaporizing process involving two elements, one may consider this system as a one component system or as a two component system with one degree of freedom fixed, i.e., the composition. The remaining degrees of freedom are the same whether one considers the congruent vaporizing system as a two component system or a one component system. For the one component system it is apparent from equation (1) that, if one has two phases present, a condensed phase and a gaseous phase, one has only one degree of freedom remaining. If one fixes the temperature there are no longer any degrees of freedom left and thus the pressure may have only one value.

When one considers incongruent processes of vaporization involving a two component system, one must distinguish between univariant and divariant systems. In the case of the univariant system a new phase is formed in addition to the original condensed phase and the gas phase. This system is said to be univariant since there are always three phases present and thus from equation (1) it is seen that there is only one degree of freedom. If one fixes the temperature there are no longer any degrees of freedom remaining and thus the pressure may have only one value.

In the case of the divariant system a new condensed phase is not formed initially by the vaporization process, but instead the composition of the original condensed phase is changed. It is apparent from equation (1) that one must have a second condensed phase present or must establish the composition of the condensed phase in order for the pressure to be fixed.

In order to determine the nature of the pressure-composition diagram two forms of experiments were conducted. The condensed phases before and after vaporization had occurred were examined by X-ray diffraction and by wet methods to determine what the composition of the vapor must have been in order to have produced the changes, if any, in the composition of the condensed phases. In the second method, a portion of the vapor was condensed and the condensate was analyzed to determine the composition of the vapor phase.

C. Effusion Method of Measurement of Pressure

There are several methods which might be used to measure the vapor pressure of a substance. Some of these methods are the static, boiling point, transpiration, Knudsen effusion (19, 20, 21), and Langmuir free evaporation (22) methods.

The vapor pressure of the compounds found was appreciable only at high temperatures. At high temperatures a vacuum is desirable to prevent interaction and to prevent the loss of power. Of the methods mentioned above only the Knudsen effusion method and the Langmuir method lend themselves to measurements in evacuated systems.

In the case of the effusion method, the vapor pressure is determined by the number of molecules of the vapor which pass through an orifice in the container. In the Langmuir method there is no container, but instead free evaporation occurs from the sample surface. Probably one of the biggest disadvantages of the Langmuir method is the inability to measure the temperature of the surface of the solid sample if it is different from that of the body of the sample. Probably the most significant disadvantage in using the Knudsen method is to find a satisfactory crucible material.

The Knudsen effusion method requires a measurement of all the vapor passing through an ideal orifice. The vapor pressures measured in this thesis were measured by collecting only that portion of the vapor from a non-ideal orifice which passed through a limited solid angle, therefore it was necessary to know the function for the angular distribution of the vapor which effused through an ideal orifice, the corrections to the function which are necessary for a non-ideal orifice, and the integration of the function for the above processes. The cosine law gives the distribution for an ideal orifice. Clausing (23, 24) has determined the corrections for a non-ideal orifice, and Freeman and Searcy (25, 26) have integrated the functions. In order to understand the limitations of the above methods, one should have a concept of the theories and assumptions which serve as the basis of the equations which are used later in this thesis.

1. Knudsen Effusion

The Knudsen effusion equation is based on the assumption that the number of molecules effusing through an orifice will be equal to the difference in the number of molecules from each side of the orifice striking the cross sectional area of the orifice. From the kinetic theory of gases the number striking the cross section from one side is given by the equation:

$$Z = \frac{n}{}\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} ts \qquad (2)$$

In the above equation,

n is the number of concentration of vapor species,

k is Boltzman's constant,

T is the absolute temperature,

m is the mass of a particle of the vapor species

t is the duration of time in which the measurement is made, and

S is the cross sectional area of the orifice.

At low pressures it is satisfactory to use the ideal gas law to determine the value for <u>n</u>, thus

$$Z = \frac{P}{2}\left(\frac{2}{\pi mkT}\right)^{\frac{1}{2}} . \qquad (3)$$

Knudsen stated that the net effusion was equal to the difference in the number from each side colliding with the orifice cross section, therefore the number effusing is

$$Z' = (2\pi mkT)^{-\frac{1}{2}}(P'-P''), \qquad (4)$$

where $\underline{P'}$ and $\underline{P''}$ represent the pressures on either side of the orifice. When the experimental details are discussed in a later section of this thesis, it will be apparent that the pressure of the gas on one side of the orifice will be negligible with respect to the other. This last statement combined with a knowledge of the molecular weight of the vapor species permits one to write the equation

$$P = \frac{W}{St} \left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}} \tag{5}$$

for the measurement of the pressure from the measurement of the mass of material which effused through an orifice. W is the mass of material which effused through the orifice and M is the molecular weight.

2. Cosine Law

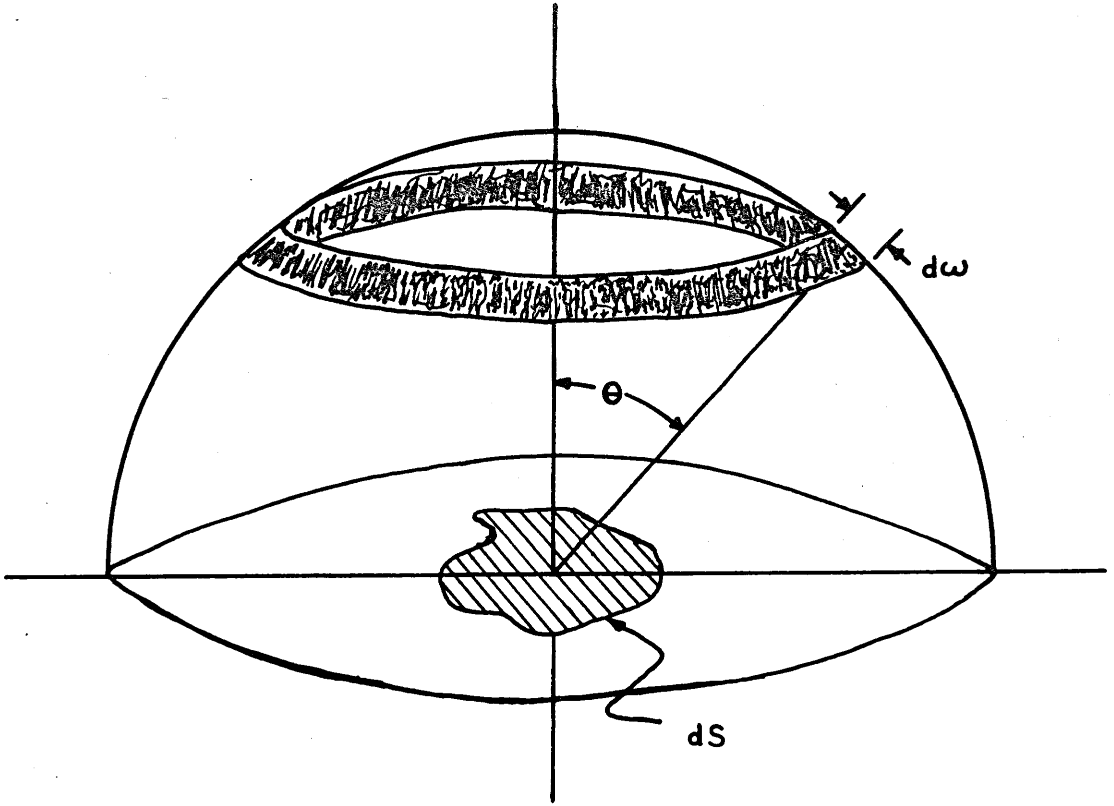
The cosine law states that the number of molecules which effuse in a direction which makes an angle θ with a normal to the cross section of an orifice will be given by

$$Z_{\theta^o} = \frac{d\omega}{4\pi} \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} tS \cos \theta, \tag{6}$$

where $d\omega$ is the solid angle whose axis is inclined at an angle of θ from the normal. Figure 1 assists one to visualize the angles involved. For an angle of zero cos θ is one, thus

$$Z_{0^o} = \frac{d\omega}{4\pi} \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} tS. \tag{7}$$

If one divides equation (6) by equation (7), one has the ratio of molecules which effuse through a solid angle inclined θ^o from the normal with respect to the molecules effusing through the solid angle whose axis coincides with the normal. The results of the division are



ANGLES PERTINENT TO COSINE LAW

FIGURE I

$$\frac{Z_{\theta^{\circ}}}{Z_{\theta^{\circ}}} = \cos \theta. \tag{8}$$

3. Clausing's Corrections

Clausing (23, 24) first considered the probability that a molecule would be effused through a tube and then he considered the angular distribution of the molecules. This is the order in which these two corrections will be discussed here.

a. Probability that a Molecule will Effuse Through a Tube

The number of molecules which pass through an orifice will be given by the equation

$$Z = W\, S\, z, \tag{9}$$

where W is the probability that a molecule will pass through an orifice if it strikes the orifice, S is the cross sectional area of the orifice, and z is the number of molecules which hit the wall per unit area. For the ideal orifice, the orifice with infinitely thin walls, W will have a value of one. Clausing assumed that the number of molecules which hit the orifice was given by the kinetic theory for an ideal gas at a pressure P. He also assumed that the molecules which hit the walls of the non-ideal orifice were restituted in accordance with the cosine law. Finally, he assumed that there was molecular flow inside the orifice. He considered the flow through the orifice to be composed of the sum of two processes. He considered that part of the molecules passed through the orifice without undergoing any collisions. The remaining molecules passed through the hole only with one or more collisions with the wall of the orifice.

Clausing calculated values for several probabilities which he incorporated into the total probability. He indicated that the total probability was equal to

$$W = \int_0^L w_{sr}(x)\; w(x)dx + w_{ss}(L). \tag{10}$$

In the above equation $\underline{L}$ is the length of the orifice, $\underline{w_{sr}(x)ds}$ is the mean probability over the cross section of the orifice that a molecule which leaves the cross section falls on a ring in the orifice $\underline{dx}$ long which is at a distance $\underline{x}$ from the cross section, $\underline{w(x)}$ is the probability that a molecule passes into a second container without returning to the first container, and $\underline{w_{ss}(L)}$ is the mean probability over a cross section area of the orifice that a molecule leaves the disk and falls directly on a second disk at a distance $\underline{L}$.

Clausing was unable to obtain a rigorous solution for $\underline{w(x)}$. He concluded that for very small values of $\underline{r/L}$, where $\underline{r}$ is the radius of the orifice, and at a sufficient distance from the end of the orifice the following equation is fairly satisfactory:

$$w(x) = x/L. \tag{11}$$

For values of r/L larger than one that the following equation is more satisfactory:

$$w(x) = \alpha + \frac{1 - 2\alpha}{L} x. \tag{12}$$

Clausing stated that if equation (12) were a true solution α would turn out to be a constant; however α was a function of x, the distance along the orifice. It was found that for large values of r/L α was practically independent of x. In considering a value for α he could have chosen a mean value, or he could have chosen values continuously over the length of the orifice.

There were certain restrictions on the choice of values for α. It was necessary to choose values such that

$$w(x) = x/L \tag{13}$$

for small values of r/L and such that

$$W = \frac{8r}{3L} \tag{14}$$

for long orifices. In order to satisfy these conditions the choice

$$\alpha = \frac{2r\sqrt{7}}{3L + 2r\sqrt{7}} \tag{15}$$

was made. The above choice for α was made to satisfy extreme conditions; however, Clausing tested the choice for intermediate value of r/L and found that it was accurate to within 2% error.

By the use of the above approximation for α, Clausing reported the following solution for the probability that a molecule would effuse through a non-ideal orifice:

$$W = \frac{1-2\alpha}{3r^2L}\left[4r^3+(L^2-2r^2)\sqrt{L^2+4r^2}-L^3\right] + \alpha + \frac{1+}{2r^2}\left[L^2-L\sqrt{L^2+4r^2}+2r^2\right] \qquad (16)$$

Demarcus and Hopper (27, 28) also have formulated, by a slightly different approach, a value for the probability that a molecule will effuse through a non-ideal orifice. They compared their values against Clausing's and found that the difference did not exceed 0.1% for a value of L/r less than two.

b. Angular Distribution of Effusing Molecules

Clausing extended the above treatment to consider the deviation from the cosine law which was caused by the use of orifices which were not infinitely thin. In order to present an equation for the deviation, he first estimated the number of molecules striking the orifice cross section at point x,

$$g(x) = z\left[\alpha + (1 - 2\alpha)\left(\frac{L - x}{L}\right)\right]. \qquad (17)$$

Once again he found it necessary to estimate a value for α. In this case, he defined it in a different fashion,

$$\alpha = \frac{\sqrt{L^2 + 4r^2} - L}{2r + \dfrac{4r^2}{\sqrt{L^2 + 4r^2}}}\,. \qquad (18)$$

Once again the equation for α is only an approximation.

It is valid only when L/r approaches zero; however, it is a very good approximation even when L is equal to $4r$.

Clausing considered the effusion of molecules in the direction z from the ring dx inside the orifice. See figure 2. He stated that only molecules passing through the shaded area of the two circles did not strike the walls of the orifice. He then combined the apparent geometrical relationship for this with the cosine law to derive an expression for the number of molecules which passed through the orifice without striking the walls of the orifice and for the number of molecules which passed through the orifice after collision with the walls. In the first case $\tan \Theta$ is less than $2r/L$, and in the second case $\tan \Theta$ is greater than $2r/L$.

The fraction effusing in the direction Θ through the solid angle $d\omega$ is given by the following:

for the first case

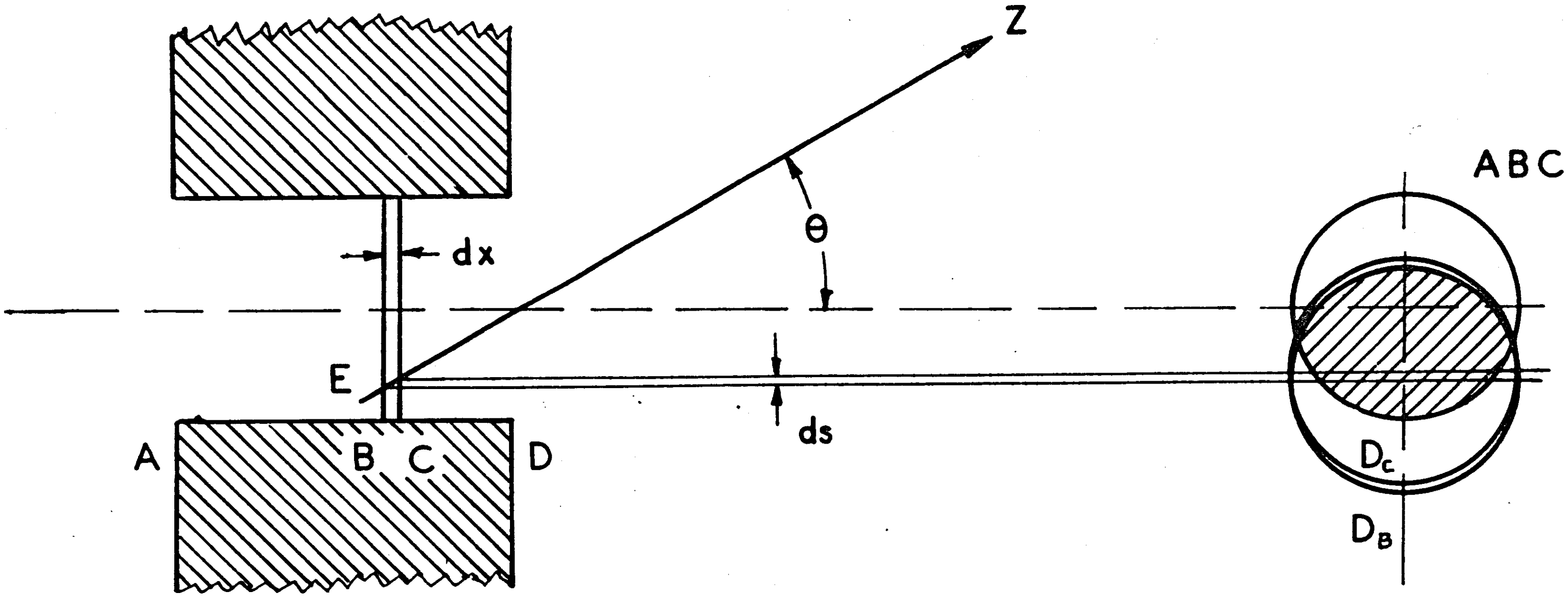
$$k(\Theta)\, d\omega = \frac{Z}{\pi} \cos\Theta \, d\omega \int_{0}^{L-4\sqrt{r^2-s^2}} \left[\alpha + (1-2\alpha)\frac{L-x}{L}\right] ds + \qquad (19)$$

$$\frac{Z}{\pi} \cos\Theta \, d\omega \, R(s)_0 \, ,$$

which after integration gives

$$k(\Theta)\, d\omega = \frac{Z}{\pi} \cos\Theta \, d\omega \, \pi r^2 \Big[1 - \frac{2}{\pi}(1-\alpha)\left(\arc\sin p + p\sqrt{1-p}\ \right) + \qquad (20)$$

$$\frac{4}{3\pi}(1-2\alpha)\frac{1-(1-p^2)^{3/2}}{p} \ \Big]$$



ANGULAR DISTRIBUTION OF EFFUSING MOLECULES

FIGURE 2

$$p = \frac{L \tan \Theta}{2r} \leqslant 1 \qquad (21)$$

for the second case

$$k(\Theta)\, d\omega = \frac{z}{\pi} \cos \Theta\, d\omega \int_{L - \frac{2r}{\tan \Theta}}^{L} -4\sqrt{s^2 - r^2} \left[\alpha + (1-2\alpha)\frac{L-x}{L}\right] ds \qquad (22)$$

which after integration yields

$$k(\Theta)\, d\omega = \frac{z}{\pi} \cos \Theta\, d\omega\, \pi r^2 \left[\alpha + \frac{4(1-2\alpha)}{3\pi p}\right] \qquad (23)$$

$$p = \frac{L \tan \Theta}{2r} \geqslant 1 \qquad (24)$$

In the above equations R(s) is the function which represents the shaded area of Figure 2.

In both cases the quantity inside the brackets is designated by T, which is the deviation from the cosine law.

If one makes a polar plot of T cos Θ as a function of Θ, one finds that the curve comes to a sharp point when Θ is equal to zero. It does not seem reasonable that the plot should come to a sharp point. Examination of the equations already presented will indicate another unreasonable consequence. There is a sharp discontinuity in the number of molecules which strike the walls of the orifice, as one approaches an infinitely thin orifice. These two discrepancies indicate that Clausing's work leaves something to be desired in the theory which enables one to calculate the deviation from the cosine law for a non-ideal orifice.

4. Freeman and Searcy's Integration

Freeman and Searcy (25, 26) were interested in the fraction of molecules, n, which effuse through a hole into a cone whose sides are at an angle, θ, with the normal to the hole. This is the problem one encounters when trying to determine the number of molecules which effuse through a hole by measuring the number which impinge upon a target a given distance from the hole. If one is able to integrate equations (20 and 23), one has the desired answer,

$$n = \int_0^\theta T \cos \theta \frac{d\omega}{\pi} . \qquad (25)$$

Equation (25) cannot be integrated analytically; however, it can be evaluated by Simpson's method, if T is known for the required values of θ. Since θ is rarely greater than 20° and usually only has values between 0° and 20°, T is nearly a linear function of θ for a given value of L/r. Freeman and Searcy have approximated T by

$$T = 1.0000 - 0.3260 \frac{L}{r} \theta. \qquad (26)$$

Combination of equations (25 and 26) and the substitution of $2\pi \sin \theta \, d\theta$ for dw upon integration gives

$$n = \sin^2\theta - 0.0815 \frac{L}{r} (\sin 2\theta - 2\theta \cos 2\theta). \qquad (27)$$

Freeman and Searcy have estimated that the accuracy of the above equation is ± 1% for values of L/r less than 2.0 and for values of θ less than 0.35. The angle θ must be expressed in radians.

D. Thermodynamic Quantities from Vapor Pressure Measurements

After the phase diagram for a particular system, the thermodynamic functions are the next most useful to characterize a system's interaction with its environment. If one knows the thermodynamic functions for the products and the reactants for the temperature under consideration, one may calculate the equilibrium constant for the reaction and determine whether the reaction under consideration can proceed to an appreciable extent if thermodynamic equilibrium is reached. There are several ways to calculate the thermodynamic functions from vapor pressure measurements.

The first of these is termed the second law method. The relationships for the Gibbs free energy,

$$\Delta F^{o} = \Delta H^{o} - T\Delta S^{o} = -RT\ln K, \qquad (28)$$

may be rearranged to

$$\ln K = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \qquad (29)$$

It will be shown in the chapter which presents the results that the equilibrium constant which is of interest is,

$$K = \frac{a\ \text{silicon}\ (a\ \text{boron})^{6}}{a\ SiB_6} \qquad (30)$$

If the activity of the SiB_6 is concluded to be unity and the activity of the silicon is equal to its pressure, one may combine equation (29) and (30) to obtain,

$$\ln P_{Si} = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} - 6\ \ln a_B \qquad (31)$$

It is apparent from the above equation that a plot of the natural logarithm of the pressure in atmospheres as a function of the reciprocal of the absolute temperature is a straight line if the enthalpy, entropy, and activity of boron are independent of temperature. It has an intercept equal to the entropy divided by the gas constant minus the natural logarithm of the sixth power of the activity of the boron. The slope of the above plot is equal to minus the enthalpy divided by the gas constant.

The enthalpy and the entropy obtained from the above processes are approximate at the temperature range of the experiments. Values at other temperatures must be obtained by the use of heat capacity data. In the event the desired heat capacity data are not available it may be estimated.

In order to obtain an enthalpy and entropy of vaporization from the above treatment it is only necessary to combine the thermodynamic values obtained with the thermodynamic values for the sublimation of silicon.

There is another way to obtain the thermodynamic quantities from measurements of vapor pressure. The entropy at the temperature of vaporization may be determined from the entropy of the reactants and the products. From the measurement of the equilibrium constant at a particular temperature, one is able to calculate the enthalpy of the process from the relationship

$$-RT \ln K = \Delta H^{o} - T\Delta S^{o} \tag{32}$$

This last method is frequently called the third law method from the manner in which the entropy is obtained.

Gilles (18) has indicated that it is not uncommon for second law values to be in error by more than ten percent. The third law value for the quantities is usually more reliable. Heat capacity data and entropy data are frequently not available and must be estimated, thus the reliability of the third law value may be impaired somewhat.

IV EXPERIMENTAL

Three basic types of experiments were performed, studies to determine the condensed phase diagram for the silicon boron system, studies to determine what vapor species existed for the silicon boron system, and lastly studies to determine the vapor pressure of SiB_6. All of the experiments were performed in a high vacuum, inductively heated apparatus.

The apparatus consisted of a crucible of either BN or ZrB_2, a susceptor of Ta or Mo, a glass envelope and support system, vacuum pumps and gauges, induction heating equipment, and a method for the measurement of temperature. For some of the experiments which involved the study of the vapor, a system of replaceable targets was used to condense and collect the vapor. The equipment will be discussed in the above order. It will be followed by a discussion of the procedures used. Finally the method of analysis for silicon and boron will be given.

A. Selection of a Suitable Crucible Material

1. Possible crucibles

The selection of a satisfactory crubicle in which to carry out the reactions between silicon and boron and to form vapor pressure measurements was one of the most difficult parts of this research. A wide variety of crucible materials, including metals, graphite, oxides, boron carbide, silicon carbide, boron nitride, and metal borides, was investigated to find ones that would meet the requirements of being relatively inert towards the chemical attack of silicon and boron and yet be sufficiently refractory at temperatures as high as 2000°C.

The refractory metals were considered as possible materials from which to construct crucibles. Molybdenum (m.p. 2625°C.), tantalum (m.p. 2996°C.), and tungsten (m.p. 3410°C.) (29) have desirable melting points. Tungsten was not used as a crucible material, since a method of fabricating a crucible from the metal was not known in this laboratory when the search was made for a crucible material. It was believed that silicon and boron would react with a crucible of either molybdenum or tantalum; however, attempts were made to use them. The boron was found to react readily with the molybdenum crucible (E1) and the tantalum crucible (E2).

The use of graphite (E3) as a crucible material was not any more successful than the use of molybdenum or tantalum, because even at the relatively low apparent temperature of 1700°C. boron was found to react more readily with graphite than silicon. When silicon was heated in a graphite crucible without the presence of boron it was found to react with the graphite to form a modification of SiC.

Since the elements did not have all of the desired properties which were required for the use of the material as a crucible, the oxides were investigated next. The use of quartz was attempted (E4). Although quartz could not be used at the higher temperatures, it was believed that possibly quartz could be used for some of the sample preparations at the lower temperatures, 1500°C. It was used a few times; however, sag was a definite problem.

The choice of alumina (E5) as a crucible material had two disadvantages. Alumina reacted with both silicon and boron to form gaseous species which were readily lost from the crucible. Alumina also apparently formed a eutectic with silicon and the bottom of the crucible was found to melt at a temperature of about 1850°C. Alumina is reported to melt at 2015°C. (30).

There was some belief that perhaps magnesia might prove to be a satisfactory material. Unfortunately, despite its high melting temperature, magnesia (E6) has a high vapor pressure which prevents its use in vacuum at temperatures in excess of 1600°C.

Zirconia (stabilized) (E7) was used as a crucible for a number of the attempted preparations of a compound between silicon and boron. ZrO_2 undergoes a change in the crystal structures when it is heated to high temperatures. The possible crystal modifications cause fabricated parts to crack when they are repeatedly heated or cooled. The crystal structure of ZrO_2 may be stabilized by the addition of small amounts of CaO. In certain instances this stabilization may be satisfactory. When attempts were made to heat boron in a stabilized ZrO_2 crucible in this laboratory, it was found that CaO was sublimed from the crucible into the boron and CaB_6 was formed.

Because the oxides were not found to be satisfactory, the other compounds were tried. It was postulated that perhaps B_4C would form a more suitable crucible, but crucibles of this material were not readily available. It was not believed to be possible to fabricate a B_4C crucible without special equipment. Attempts were made to coat the inside of a graphite crucible with sufficient boron to form a coating of B_4C which would be inert with respect to attack by boron, or silicon, or any compound that silicon and boron might form with each other. In all cases the graphite which absorbed the boron in the process of forming the B_4C had a tendency to expand, and this resulted in the rupture of the walls of the graphite crucible.

Recently self bonded silicon carbide crucibles and nitride bonded silicon carbide crucibles have appeared on the market. At the time when a crucible material was being sought, the only SiC crucibles that were available were silicon bonded and graphite bonded (E8). The graphite bonded crucibles were perhaps not as good as pure graphite, since they possessed the same reactivity but lacked the structural strength of graphite. The silicon bonded crucibles (E8) suffered from similar disadvantages. After silicon carbide was examined as a possibility, more was learned about the sintering of powders to form usable crucibles. It might have been possible to fabricate readily a nitride bonded or self bonded silicon carbide crucible.

2. Boron Nitride Crucibles

Boron nitride was found to possess some of the most useful characteristics, and it was used for the preparative work. Not only was it inert towards reaction with silicon and boron, but in addition the molten silicon did not wet the boron nitride. The boron nitride was obtained from the manufacturer in the form of 3/4 inch rods (E9), but it was readily fabricated into crucibles and lids. It is possible to machine boron nitride about as readily as one machines graphite.

The decomposition of BN becomes appreciable at higher temperatures. In order to prevent this decomposition, attempts were made initially to use the BN crucibles in a nitrogen atmosphere. This was an unsatisfactory arrangement, since the nitrogen atmosphere reacted with the material in the crucible to form nitrides. It was later found that the BN crucible could be used at temperatures as high as 1700°C.; however, at this temperature a vacuum of only about 1×10^{-4}mm. of mercury could be obtained in the vacuum system. This pressure presented no great problem for sample preparations, but it rendered the BN useless for use in the measurement of the vapor pressure of SiB_6.

It was found necessary to heat the BN crucibles in vacuum before using them. The BN supplied by the manufacturer was contaminated with some form of calcium, and when the BN was heated the calcium was sublimed into the sample.

3. Metal Boride Crucibles

It was believed from the first that the use of a refractory boride of titanium, zirconium, or tantalum would prove to be satisfactory. All of these materials already contained boron and have relatively high melting points. TiB_2 melts at ca. 2600°C.; TaB_2 decomposes to form other borides at temperatures above 2000°C.; and ZrB_2 melts at 2990-3000°C. (31) After the phase diagrams for the three compounds had been compared (5), it was concluded that ZrB_2 would be the most stable with respect boron attack.

Crucibles of the above materials were not available commercially and, initially, no attempt was made to fabricate them. It was believed that in order to accomplish sintering of the above refractory borides, one would have to heat the material to a temperature which was higher than the temperatures attained in this laboratory.

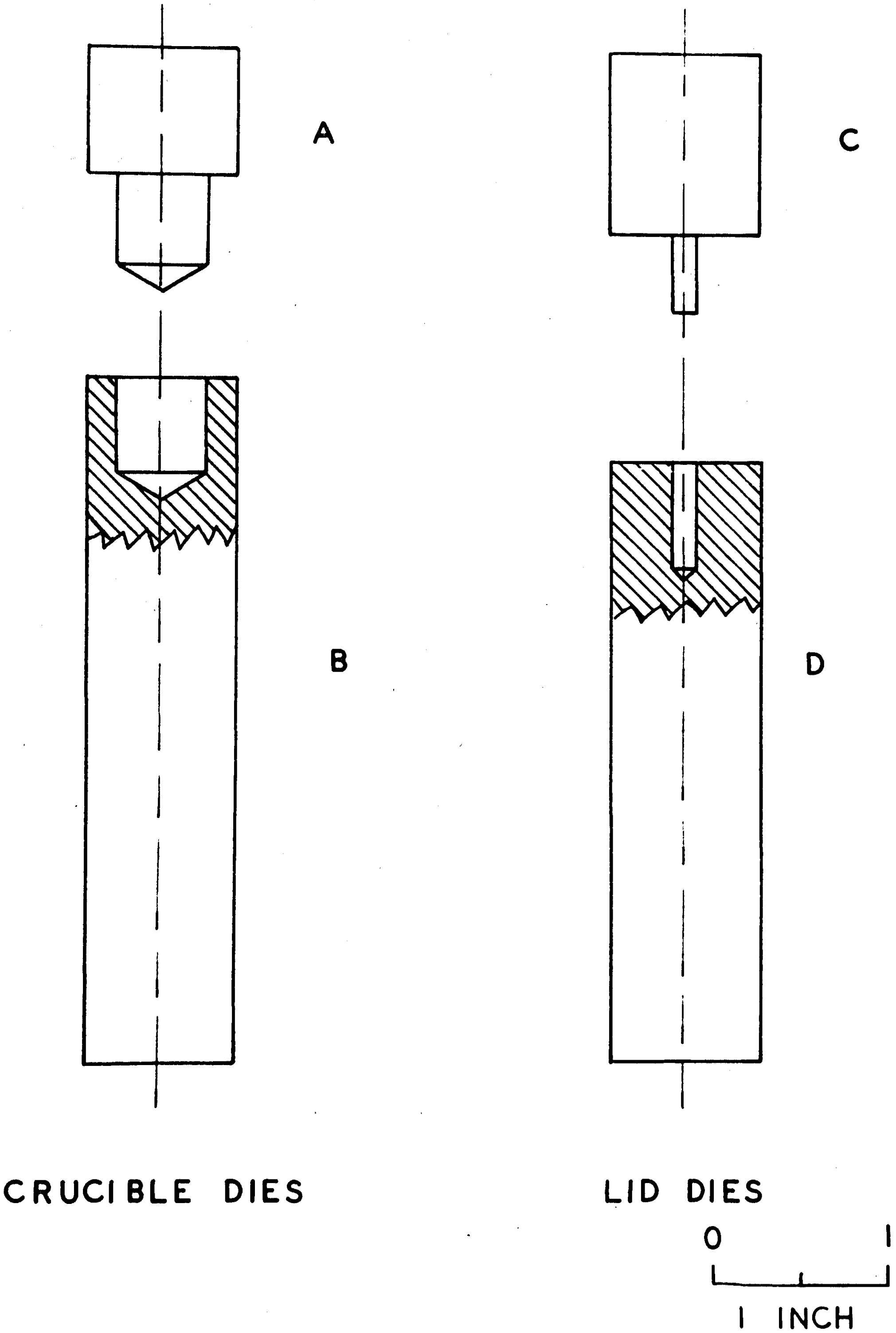
In the first attempts to fabricate a crucible of TaB_2, mixtures of tantalum and boron were pressed into the desired shape and heated to initiate reaction between the tantalum and the boron. This was not a satisfactory method. The tantalum reacted so vigorously with the boron that much heat was generated and the shape was destroyed by the expanding gases. Attempts were made to increase the applied heat slowly to prevent the vigorous reaction, but the vigorous reaction persisted. Diluting the tantalum and the boron with TaB_2 was also not successful in decreasing the disintegration of the form before it had sintered.

Since the shape of the material could not be maintained in the above experiments, attempts were made to hot press the desired shapes. The material was held inside a graphite mold, the pressure was applied by a laboratory press (E10), and the mold was heated by induction heating. This arrangement was more successful than the heating of the unrestricted form. Hot pressing had the disadvantage that it was most difficult to remove the product from the mold, because part of the boron reacted with the graphite mold instead of with the tantalum. With the hot pressing arrangement described above, it was only possible to attain a temperature of 1200°C. and a pressure of ca. 1000 p.s.i. When higher pressures were placed on the graphite plungers of the apparatus, they were crushed.

It was found finally that a semi-satisfactory crucible of rigid form could be obtained by heating TaB_2 after it had been pressed into the desired shape. The problem usually associated with such an operation is the removal of the pressed-powder shape from the dies. Occasionally one also finds that the material will crack while it is being heated to the temperature at which sintering occurs.

It was found that the problem could be solved by using the following procedure: The powder was moistened with a few drops of water before it was pressed. The faces of the dies were lined with weighing paper which facilitated the form to be slipped from the dies. Finally the form was pressed by stages, i.e., only enough material was added to form the sides and only after the sides had been pressed was more material added to be pressed into a bottom. Sintering of the crucible was accomplished by heating the material for one hour at 2000°C.

Figure 3 is a sketch of the dies used. They were fabricated from cold-rolled steel rods. Note that the end of plunger B was used to press the walls and the other end was used to press the bottom. Plungers C and D were used to form one of the lids which were used in the effusion experiments. Dies of different dimensions were used to form the other lid which was used in the effusion experiments.



CRUCIBLE DIES

LID DIES

CRUCIBLE AND LID DIES

FIGURE 3

It was anticipated that TiB_2 could also be sintered, but the surprising finding was that ZrB_2 could be sintered without the necessity to exceed 2000°C. It was found that the ZrB_2 was sintered sufficiently after it had been heated for two hours at 2000°C. The zirconium and titanium borides were obtained commercially (E11, E12); however, the tantalum boride was prepared in this laboratory from tantalum and boron (E13, E14).

After the availability of either a TiB_2, TaB_2, or ZrB_2 crucible was realized, the problem was which of the borides would be the least likely to react with silicon, or boron, or their compounds. The problem was solved in a rather simple fashion. By the time it was realized that a refractory metal boride could be formed into a crucible, SiB_6 had already been prepared in a BN crucible. Mixtures were prepared between each of the borides and the SiB_6. The mixtures were pressed into plugs and heated one at a time in the TaB_2 crucible for 30 minutes at 1715°C. An X-ray diffraction pattern (E15) was prepared of the material before and after the heating. The appearance of additional lines in the films taken after the heating was considered as evidence of interaction.

TaB_2 displayed the most reaction with the SiB_6; however, no reaction appeared to occur between the ZrB_2 and the SiB_6. The reaction products between the refractory borides and SiB_6 were not identified.

B. Crucible Design

It was possible to make a relatively tight fitting lid for the BN crucible; however, the vapor pressure of the BN was appreciable. The vapor pressure of the ZrB_2 was negligible; however, a tight fitting lid could not be fashioned from this material, because neither the tolerances could be maintained during the sintering process, nor could the resulting piece be machined. Since a tight fitting lid was necessary for the sample preparations to prevent the loss of silicon, the BN crucible was used for this purpose. Since the vapor pressure of BN could not be tolerated when the vapor pressure of SiB_6 was measured, the ZrB_2 crucible and two different lids with orifices of approximately 1/16" and 1/8" were used for this purpose.

In a later section the use of induction heating will be described. Neither BN nor ZrB_2 will heat inductively; therefore, it was necessary to surround the material with a susceptor which could be heated by induction. The hot susceptors heated the BN and ZrB_2 crucibles by radiation. Tantalum was used to heat the ZrB_2 and molybdenum was used to heat the BN. Both were equally well suited; therefore, the choice was made on the basis of the availability of the desired shapes which were required.

Theoretically in order to have the crucible and the lid at a uniform temperature, it is necessary to surround them completely with a susceptor at a uniform temperature. In order to try to accomplish this, covers which also heated inductively were placed on top of the susceptors.

In order to prevent interference with the vapor effusing through the orifice of the ZrB_2 lid, it was necessary to provide a hole in the susceptor cover which was used with the ZrB_2 crucible and lid. The hole had to be small enough to prevent the lid from becoming cooler than the crucible. On the other hand, the hole had to be as large as possible to prevent the susceptor cover from interfering with the beam of the molecules effusing through the orifice. If the distribution were disturbed, equation (27) would not give the fraction collected.

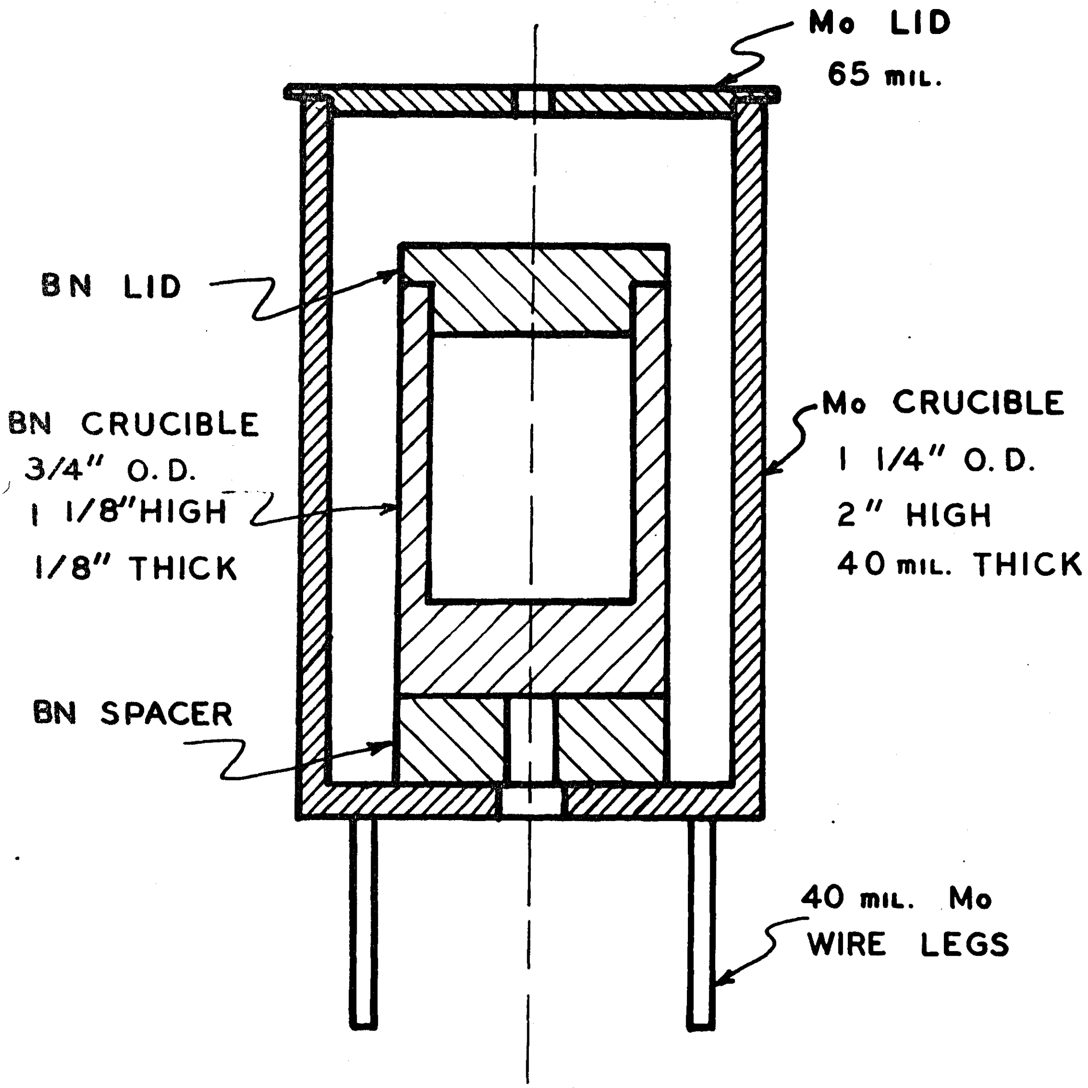
In order to decide what size hole should be made in the susceptor cover, several covers were designed and used. The one that was selected for the effusion measurements had a hole just small enough to prevent the vapor from depositing in the orifice, yet the hole was sufficiently large that no vapor could be observed on the under side of it after its use. It will be shown later that it was necessary to have two lids for the ZrB_2 crucible. Since the lids had different size holes and were of different thicknesses, a susceptor was provided for each lid.

Since less power was generated in the bottom of the susceptor than in the sides, the bottom of the susceptor was cooler than the sides. In order to separate the crucibles from the bottoms of the susceptors, a disc was fashioned from the same material as the crucibles and the crucibles were supported by these discs. In order to measure the temperature of the bottom of the crucible, a hole was provided in the bottom of the susceptor and in the supporting disc.

Figure 4 is a diagram of the BN crucible inside the molybdenum susceptor. Figure 5 is a diagram of the ZrB_2 crucible and one of the lids and susceptors which were used with it.

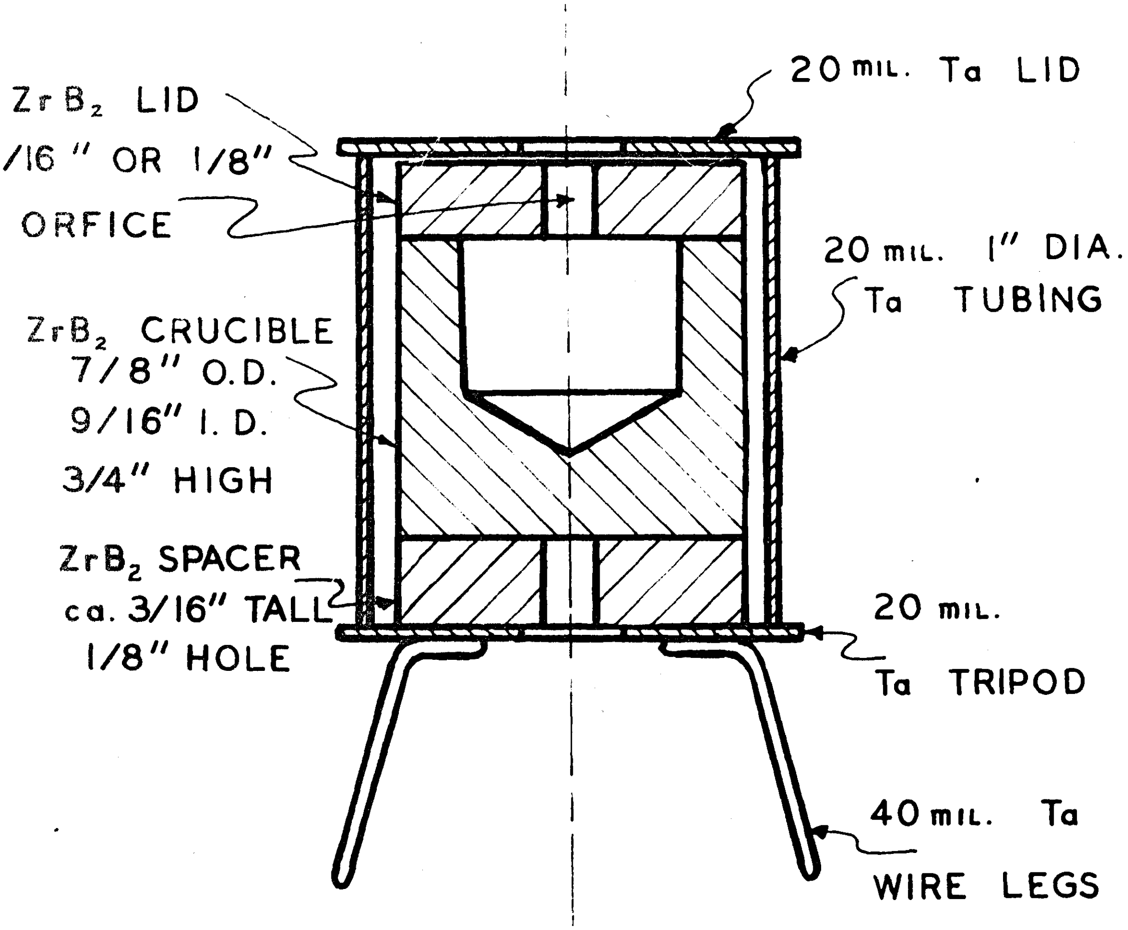
C. Support System

The susceptor which contained the crucible was supported on a semi-kinematic quartz table. The table was constructed from a cylindrical quartz blank (E16). Cut across the top of the blank were grooves which intersected in the center of the top to form angles of 60° with one another. A glass saw and a specially designed jig were used to facilitate the cutting of the grooves. The table rested on top of a Vycor tube which was sealed to the glass envelope. A circular groove was cut into the bottom of the quartz table to prevent it from sliding on the support tube.



BN CRUCIBLE INSIDE Mo HEATER

FIGURE 4



ZrB_2 CRUCIBLE INSIDE Ta HEATER

FIGURE 5

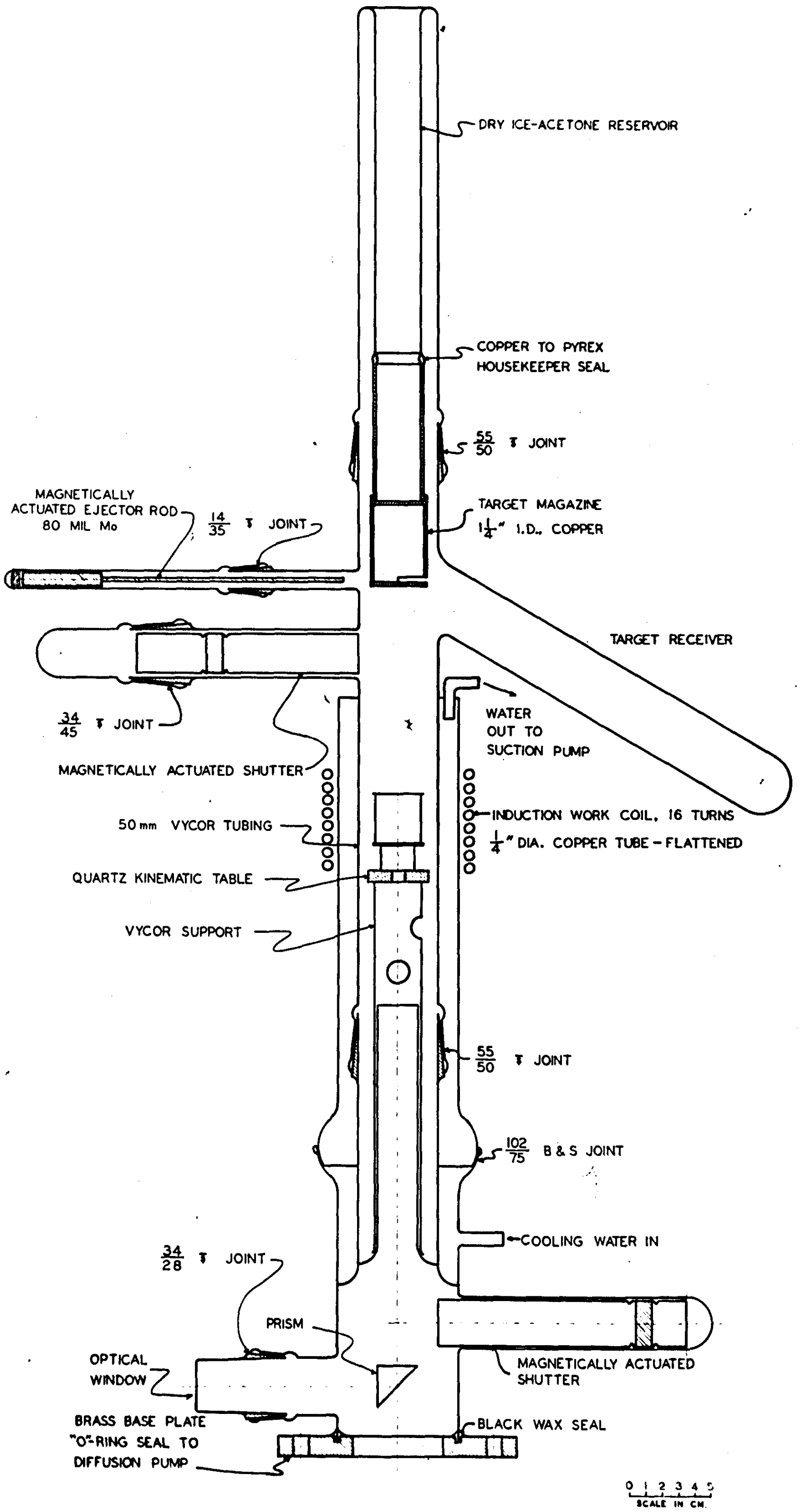
D. Sample Preparation Apparatus

The sample preparation apparatus was constructed of Pyrex and Vycor. The lower Pyrex part was connected to the cold trap of the diffusion pump. It was 75mm. in diameter and was joined to a 55/50 standard taper joint. A side arm was sealed to this section to provide an optical window. Through the optical window and a prism which was contained in this section could be observed the bottom of the crucible. A glass shutter which could be operated by a magnet outside the glass envelope could close over the prism and prevent its transmission characteristics from being changed. The Vycor support tube of the support assembly was connected to this lower section of the glass envelope. This section of the glass envelope was common to this apparatus and the effusion apparatus which will be described in the next section.

The upper half of the glass envelope consisted of a vertical condensor which connected to the lower half. This condenser was a standard wall thickness 51mm. Vycor tube 480mm. long closed at one end and sealed to a 55/50 standard taper joint at the other.

E. Effusion Apparatus

The effusion apparatus consisted of a system of replaceable targets and a Pyrex and Vycor envelope. Figure 6 is a schematic diagram and Figure 7 is a photograph of



EFFUSION APPARATUS

FIGURE 6

EFFUSION APPARATUS

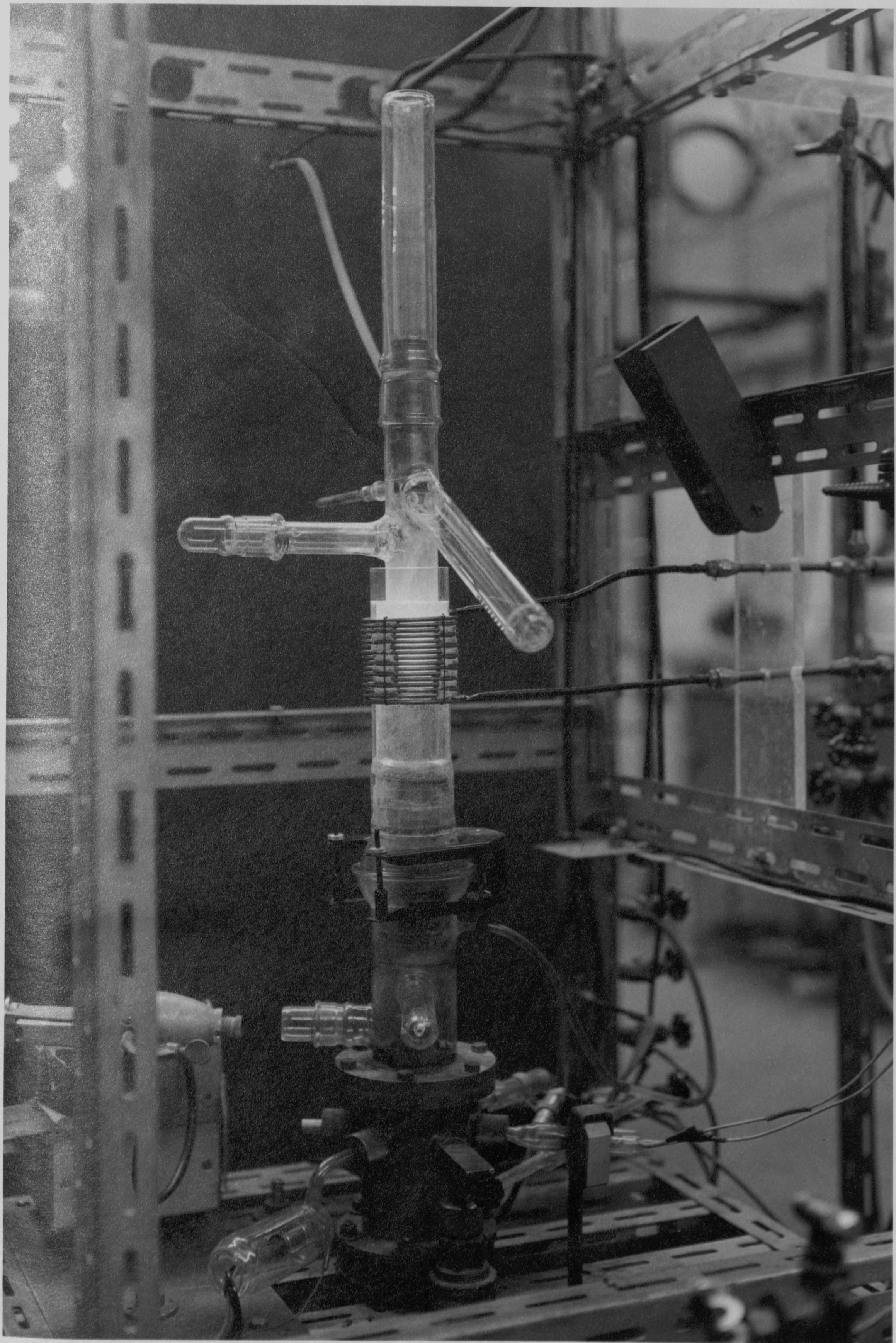


FIGURE 7

the effusion apparatus. The crucible, susceptor, semi-kinematic table, supporting tube, and lower portion of the glass envelope have already been discussed.

It will be noted in Figure 6 that certain of the parts have been specified to have been constructed of Vycor. The remaining glass parts were constructed of Pyrex. The 50mm. standard wall Vycor tube was of such a length that the bottom of the magazine was 135.5 mm. above the top of one of the two crucible lids.

The copper target magazine could hold up to six targets for subsequent exposure. The lower retaining ring of the magazine was beveled on the lower edge of the inner periphery so that a knife edge was formed at the top surface. This knife edge served to fix more definitely the fraction of vapor which was permitted to strike the target. The target was contained in a supporting ring which rested on the collimator ring.

A plunger which could be actuated by a magnet outside the glass envelope consisted of a molybdenum rod affixed to an iron slug. A system of holes in the target magazine enabled the plunger rod to strike the supporting ring which held a target and to push the ring and target out the side of the magazine and into the target receiver. After the ring was ejected another ring and target dropped into position.

A glass shutter which also could be operated by a magnet was positioned below the target magazine. This shutter could be closed to prevent vapor from striking the targets. Thus, one could adjust the temperature of the crucible before a target was exposed. The use of a shutter also enabled one to fix more definitely the time of the exposure of the targets.

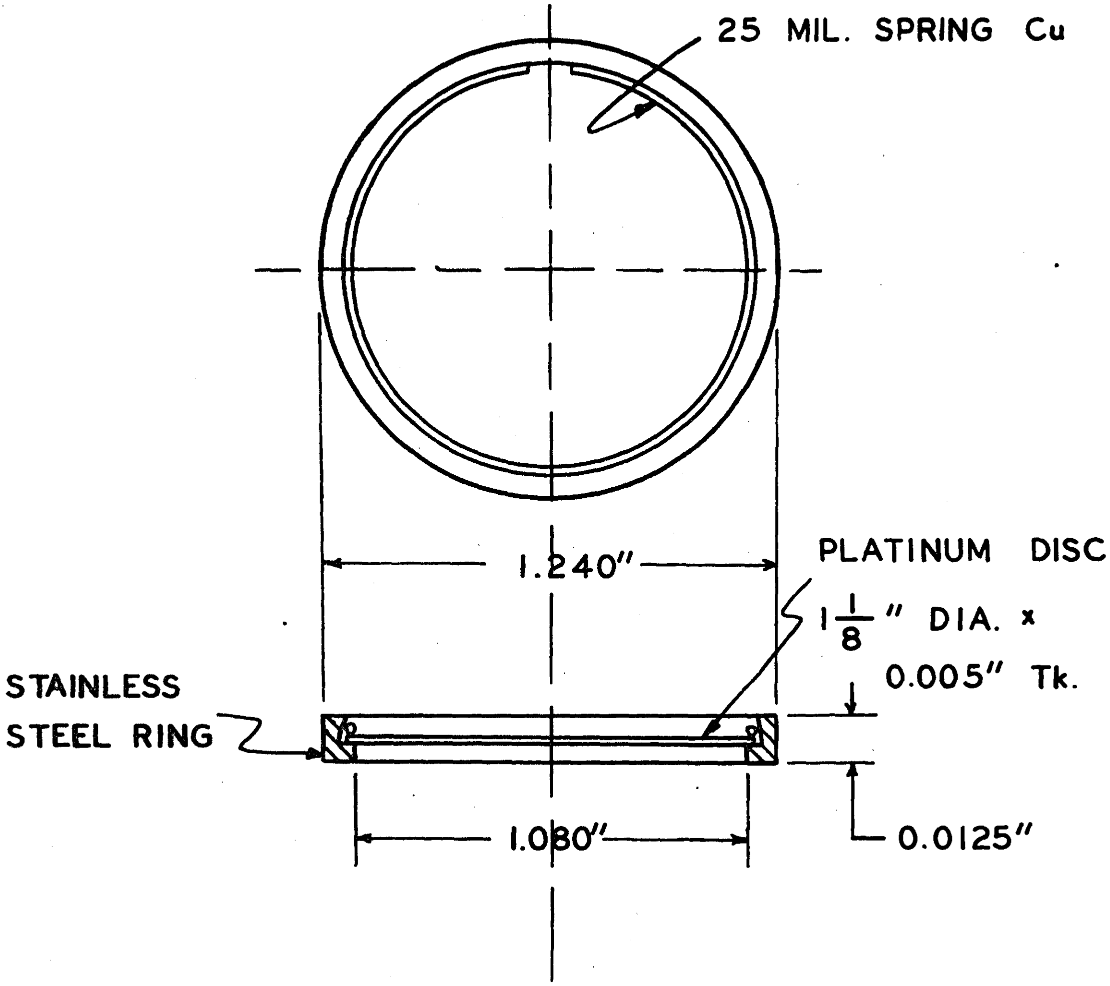
The target rings were cooled by contact with the copper magazine which was in turn cooled by dry ice acetone refrigerant contained in the reservoir directly above the target magazine.

The targets consisted of platinum discs 1 1/8 inches in diameter held in supporting rings of stainless steel by 22 gauge spring copper wire. A diagram of the target assembly is shown in Figure 8.

F. Vacuum Pumps and Gauges

It was necessary to conduct the heatings in vacuum to insure a mean free path of the vapor sufficient to prevent collisions of the effusing species with itself before it strikes the target. The vacuum technique also eliminates heat losses by conduction and convection and contamination by atmosphere.

A dry ice acetone cold trap was provided above the diffusion pump to prevent oil from diffusing into the apparatus. The trap consisted of a group of brass baffles.



TARGET ASSEMBLY

FIGURE 8

The vacuum was attained by means of a mechanical fore pump (E17) and an oil diffusion pump (E18). The standard taper glass joints of the glass envelope were rendered vacuum tight by the use of high vacuum stopcock grease (E19). The metal to metal seals were facilitated by the use of neoprene "O" rings (E20). The copper to glass seals were purchased (E21). "Black wax" (E22) was used to make the glass to brass seal at the bottom of the effusion apparatus.

The vacuum attained was measured by means of a pirani gauge (E23), a cold cathode gauge (E24), and a logarithmic ion gauge (E25). The pirani gauge was used to measure the pressures from one atmosphere to one micron and the cold cathode gauge and the logarithmic ion gauge were used to measure pressures from one micron to 10^{-7} mm. of mercury.

For the effusion measurements, it was possible to obtain a vacuum of 1×10^{-6}mm.; however, when the BN crucible was used at high temperatures a vacuum of only 1×10^{-4} mm. could be obtained.

G. Induction Heating

The crucibles were heated by the radiation of heat from susceptors which were heated by induction. Induction heating has a number of advantages. The heating occurs much more rapidly than other methods since the heat is generated within the body itself. There is no need to pass conductors through the vacuum envelope. Finally, the region that is heated is axially restricted to the region within the primary work coil.

If one neglects the power losses in the primary work coil, one would find that the heat generated in the sample is proportional to the frequency. Because power losses in the circuitry increase with the frequency, there is an optimum value for the frequency. The frequencies used for induction heating are also restricted, because of the reservation of certain frequencies for radio communications.

A 20 kw. vacuum tube oscillator (E26) was used as a power supply for the induction heating. It had a rated frequency of 500 kc. The work coil had a fairly high impedance because of the number of turns which were necessary to attain sufficient coupling with the susceptor. This necessitated the use of a minimum grid pickup, therefore it was possible to obtain a frequency of only 390 kc. The low frequency did not impose a serious disadvantage on the maximum temperatures which could be obtained. It was never found necessary to use a power setting of more than 75% of full power.

The power supply was controlled by means of the variation of the bias to the thyratron tubes in the rectifier section of the oscillator. The bias was controlled by a variable 10KΩ resistor in series with a variable 1KΩ

resistor serving as a vernier for the larger resistor. To insure a more nearly constant power delivery the voltage to the vacuum tube oscillator was regulated by means of dry-type induction voltage regulators (E27). A measure of the performance of the power supply is that the temperature would not change during one hour for a given power setting more than four degrees at a temperature of 1200°C.

The primary work coil consisted of 1/4 in. flattened copper water tubing fashioned into sixteen turns with an inside diameter of 75 mm. and a height of 70 mm. The turns were insulated from one another by asbestos paper.

H. Temperature Measurement

Temperature measurement was accomplished by means of an optical pyrometer (E28) which had been calibrated by the National Bureau of Standards, test no. G24954, 31 March 1959.

It is not sufficient to measure the temperature of an object by sighting on it through the telescope of an optical pyrometer and matching the brightness of the filament with the brightness of the crucible. Corrections had to be made for the fraction of the light that was reflected and absorbed when the light passed through the window and prism which were necessary in these experiments. In addition, the possibility had to be considered that the bottom of the crucible on which the pyrometer was sighted might not be at the same temperature as the contents of the crucible. There was also the possibility that an emissivity correction should be applied to the temperature as determined by the material of the crucible.

A discussion of the window and prism corrections will now be made. For correction purposes the prism (E29) and the window (E30) were considered as a single unit, since at all times one did not sight through one without sighting through the other. They were considered as a single screen which absorbed a fraction of the light emitted by the crucible.

The absolute true temperature of a body T_t may be calculated by measuring the apparent temperature T_a through a neutral screen and calculating the true temperature from equation (33) which is derived from Wein's law.

$$1/T_a - 1/T_t = - \frac{\lambda_e}{C_2} \ln \tau \qquad (33)$$

In the above equation λ_e is the effective wave length, C_2 is Wein's second constant, and τ is the fraction of light transmitted.

The right side of the above equation may be considered as a constant for purposes of calibration of windows and prisms. The quantities C_2 and τ are true constants. For an optical pyrometer similar to the one used in these experiments, the effective wave length was found to vary from 0.6512 to 0.6523 for the temperature range used.

The effective wave lengths were calculated by assuming that the temperature differences were 50°C. Since it was possible to evaluate the right side of the equation to only two significant figures, it was considered satisfactory to regard $\underline{\lambda_e}$ as a constant.

It was necessary to evaluate the right side of equation (33) several times during the research. Calibration was accomplished by the use of a second vacuum system similar to the one described previously. A graphite cylinder with a black body hole was heated with the induction heating equipment. The temperature of the body was measured in the normal manner and this measurement was considered to give a value for $\underline{T}_t$. The temperature of the body was then measured by placing the window and the prism in the path of the optical pyrometer. This temperature was used as a value of $\underline{T}_a$ which was combined with $\underline{T}_t$ to give the value of the right hand side. These measurements were measured three times at each power setting. The power was adjusted so that temperature measurements might be made at 50° temperature intervals over the temperature range which was used in these measurements. Initially attempts were made to calibrate the window and prism by sighting on the filament of a projection lamp. It was found that the temperature of the graphite body was more constant than the filament and that it was easier to match the brightness of the filament to the brightness of the black body hole of the graphite cylinder than to the brightness of the surface of the filament.

Mention has already been made of the shutter which protected the prism from the depositation of vapor from the susceptor and crucible. It was necessary in order to prevent a coating that would decrease the percentage of light transmitted through the prism and thereby void the calibration.

Table I shows the data gathered for a typical calibration of the value for the right side of equation (33).

TABLE I

CALIBRATION OF WINDOW AND PRISM

Average Temperature Degrees Kelvin		Constant Calculated 10^{-5} deg^{-1}
With Window and Prism	Without Window and Prism	
1739	1771	1.04
1780	1820	1.23
1833	1876	1.25
1876	1922	1.28
1929	1973	1.15
1970	2023	1.33
	mean	1.21
	probable error of mean	±0.028

When this section was introduced mention was made of the possibility that the temperature of the sample was not equal to the temperature of the bottom of the crucible. It has already been stated that the major thermal gradients occurred at the ends of the susceptor and that the top and the bottom of the susceptor were closed to prevent the loss of heat by radiation. The use of a disc to separate the crucible from this region of temperature gradient has been indicated, therefore the assumption was made that the temperature of the bottom was the same as that of the sample.

In order to measure the true temperature of a body with an optical pyrometer, one must have black body conditions or apply some correction to the measured temperature to convert it to the true temperature. In these experiments the temperature measurements were made by sighting through the supporting spacer and onto the bottom of the crucible. The supporting spacer was intended to simulate a black body hole.

A test was made to determine if the disc did create a black body hole. It was concluded that by sighting through the orifice down into the crucible did represent observing the temperature of a black body hole; therefore, by means of a window and prism above the crucible and a prism and window below the crucible a comparison of the temperature measured by the two methods was made. At 1739° the difference in the two temperatures was found to be negligible; however, at a temperature of 1987°K, it was found that the temperature read from the bottom was nine degrees low. The appropriate corrections were made to the temperatures measured from the bottom of the crucible.

I. Determination of Phase Diagrams

Now that the apparatus used has been discussed, the actual procedure used to determine the phase diagrams will be presented.

The temperature composition diagram was determined by heating samples of various compositions in closed crucibles to fixed temperatures. The phases were noted which were present in the sample after it had been cooled. The decomposition temperatures were verified by making successive heatings at increasingly higher temperatures until evidence of the decomposition products could be detected in the samples after they had been cooled.

Two methods were used to determine the nature of the pressure composition diagrams. Samples were heated at various constant temperatures in open crucibles and the condensed phases were examined before and after the heatings. The nature of the vapor phase was deduced from the changes in the condensed phases. In the second type of experiment the platinum targets were used to condense some of the vapor. The deposit on the targets was examined to determine the ratio of silicon to boron which had been present in the vapor.

The silicon used in the preparations was represented by the manufacturer to be "solar grade" (E31). The amorphous boron used was represented by the manufacturer to be 99.2% pure (E14). The analysis submitted by the manufacturer for the boron listed the impurities, but no mention was made of any oxygen impurity. An analysis in this laboratory indicated that the amorphous boron was only 97.2% pure. The difference may or may not have been the presence of oxygen in the boron. The method of analysis of both the silicon and the boron will be explained in a later section of this thesis.

To insure the completion of the reaction the silicon was powdered with a mortar (E32) sufficiently to pass through a 325 mesh sieve (E35). To prevent the loss of silicon during reaction, all of the preparations were carried out in BN crucibles.

After the samples had been heated as rapidly as possible and cooled by discontinuing the supply of power, the material was examined by both X-ray diffraction (E15) and wet analysis. It was found necessary to grind the samples for X-ray diffraction in a boron carbide mortar and pestle (E34) to prevent contamination. The wet analysis was necessary even for the samples for which no effusion was planned. Some silicon was lost even when the BN crucible and lid were used.

It was found necessary to heat the samples for a longer period of time at the lower temperatures in order to establish equilibrium. At the lower temperature, 1227°C., some of the samples were annealed for eighteen hours. At the higher temperatures, 1860°C., the samples were annealed for only a half hour. During the annealing process the temperature was maintained to within ± 5°C.

The problem of the attainment of equilibrium was an interesting one. At the higher temperatures this was not a problem, since the variation of the heating from one half to two hours had no effect on the products formed. At the lower temperatures some erroneous conclusions were made with regard to the nature of the phase diagram before it was realized that longer heating of the samples did have an effect on the products formed. Heating was continued at the lower temperatures until no change was observed in the products formed.

J. Measurement of Vapor Pressure of SiB_6

The Knudsen effusion apparatus which was used to measure the vapor pressure of SiB_6 has already been described. An account will now be given of the procedure which was used.

It was necessary to prepare a new sample each time the crucible was filled for the effusion studies. It was necessary to fill the ZrB_2 crucible almost full for each group of pressure measurements. Since the capacity of the

ZrB_2 crucible was about the same as the capacity of the BN crucible, all of one preparation was used to fill the crucible.

When the ZrB_2 crucible had been filled it was possible to expose about five targets before the sample became depleted of SiB_6. The condensed phases in the crucible were examined before and after the vaporization for the presence of two condensed phases.

In the event this criterion was not met the pressure measurements for the sample were disregarded. From what has been said in the theoretical chapter and the description of the apparatus, it is apparent that only a fraction of the vapor was condensed on the platinum targets. The vapor pressures were calculated by the use of the following equation,

$$P = \frac{W}{KStn} \left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}} , \qquad (34)$$

in which,

W is the weight collected on the target in grams,

S is the area of the orifice in cm^2,

t is the time of exposure in seconds,

R is the gas constant, 8.3136×10^7 ergs/deg. K-mole,

T is the temperature in degrees Kelvin,

M is the molecular weight of effused species in grams/mole, n is the fraction collected and is dimensionless, and

K is a factor to convert the pressure to atmospheres,

$K = 1.01325 \times 10^6$ dynes/cm^2-atmospheres.

The quantity n was calculated from the following equation:

$$n = \sin^2 \theta - 0.0815 \left(\frac{L}{r}\right)(\sin 2\theta - 2\theta \cos 2\theta) \qquad (35)$$

in which,

θ is the angle between a normal drawn to the plane of the lid and a line drawn from the center of the orifice to the defining edge of the collimating ring,

L is the length of the orifice, and

r is the radius of the orifice.

The method of measurement of the weight of material collected on the platinum target will be discussed in a separate section. The method of temperature measurement has already been discussed. The method of measurement of the other quantities listed above will now be made.

Two ZrB_2 lids were used to make the effusion measurements. The orifice of the one lid was approximately four times the area of the orifice of the other lid. The purpose of the two area sizes was to determine if the vapor pressure was a function of the area of the orifice. If the vapor pressure measured using the larger orifice was smaller, this would indicate that the vapor in the crucible was not saturated when the larger orifice was used.

The area of the orifices were measured by the use of a comparator (E35). In order to correct for the possible lack of circularity of the orifice, the diameter was measured in two directions perpendicular to one another. Table II shows the precision which was obtained in measuring one of the orifices. In the event that the diameter changed as a result of depositation of silicon in the orifice the pressure measurements were disregarded.

TABLE II

DIAMETER OF ORIFICE, LID I

	Direction A	Direction B
	3.1142 mm	3.1297 mm
	3.1207	3.1283
	3.1230	3.1294
mean	3.1192 mm	3.1291 mm
probable error	±0.0018 mm	±0.00028 mm

Table III indicates the precision that was obtained in measuring with a micrometer (E36) the thickness of one of the lids.

The precaution of measuring the diameter in two directions was used in measuring the collimator ring of the target magazine. The collimator was measured by means of a vernier caliper (E37). Table IV gives an indication of the precision obtained.

TABLE III

LENGTH OF ORIFICE, LID I

	0.201 in.
	0.199
	0.199
mean	0.1993
probable error of mean	±0.00015

TABLE IV

DIAMETER OF COLLIMATOR

	Direction A	Direction B
	0.939 in.	0.940 in.
	0.938	0.940
	0.939	0.941
mean	0.9386	0.9403 in.
probable error of mean	±0.00022	±0.00022

The height of the defining edge of the magazine above the top of the lid was measured by means of a cathetometer (E38). It was necessary to make this type of measurement for each lid, since the two lids were of slightly different thickness. Table V gives an indication of the precision obtained. Since the inside top of the bottom retaining ring served as the defining edge, it could not be observed directly. The outside top of the ring could be observed where it had been joined to the copper tube. It was assumed that the ring had not been deformed in the process of fabrication, therefore the outside was used as a point from which to measure.

TABLE V

HEIGHT OF COLLIMATOR ABOVE TOP OF CRUCIBLE LID, LID I

	Collimator		Top of Lid
	91.43 mm. 91.39 91.42		77.61 mm. 77.57 77.55
mean	91.413 mm.		77.577 mm.
probable error of mean	±0.026 mm.		±0.012 mm.
difference		13.836 mm.	
probable error of difference		±0.029 mm.	

The time was measured by observing the time interval as indicated by a digital timer (E38). The timer was capable of indicating the time to one hundredths of a minute. The time was observed immediately after opening the shutter that protected the target and immediately after the shutter was closed. It was assumed that the time lag was the same in both instances. The same degree of difficulty was associated with opening and closing the shutter.

Before the platinum targets were used to condense vapor it was necessary to remove all traces of silicon and boron from them. As a test of the cleaning procedure, platinum targets were used which had been exposed to silicon vapor. Initially it was believed that the silicon could be removed from the targets by heating them in atmosphere. Even when the targets were heated to a temperature just below the melting point of platinum, the silicon was not vaporized. It was found that fused Na_2CO_3 could be used to clean satisfactorily the targets before they were used to condense vapor.

In order to determine what molecular weight to use for the vapor, the work of Honig (32) and the corrections to his work (33) were considered. In his work he reported the ratio of the diatomic species to the monatomic. From his report the monatomic-diatomic equilibrium constant was calculated. From the equilibrium constant the ratio was calculated for the pressure of silicon in equilibrium with SiB_6 (s) at 1650°C., and it was found that the vapor consisted of 0.013% diatomic molecules. This amount was considered to be negligible, therefore the molecular weight of the vapor species was considered to be 28.06.

The identification number of each effusion measurement was composed of two numbers. The first half of the number was the number of the note book page on which the series was initiated. The second half of the number was the number engraved on the target retaining ring. The targets were placed in the magazine so that they would be exposed in increasing numerical order.

K. Silicon Analysis

The method of silicon analysis was modified from a molybdenum blue colorimetric method which was presented by Charlot and Bezier (34). It was necessary to determine the silicon concentration in the samples which were used in the phase studies. In addition it was necessary to determine the amount of silicon which had condensed on the platinum targets.

Approximately ten milligram samples were used for the analysis of the material from the phase studies. The sample was mixed with two grams of Na_2CO_3 and fused at the full heat of a meeker burner for thirty minutes. The sample was then transferred to a volumetric flask and diluted to 100 cc. In order to have a sample with approximately the same amount of silicon and the same amount of Na_2CO_3 in it, an aliquot was taken which contained from 50 to 150 micro grams of silicon and was mixed with three grams of Na_2CO_3. This permitted the use of the same calibration for samples arising from the two different sources.

For the analysis of the amount of silicon on the targets, the target was placed in a platinum dish and covered with three grams of Na_2CO_3. The sample was heated at the full heat of the meeker burner for thirty minutes. After the sample had cooled it was dissolved in about ten cc. of water. From this point on both samples were treated the same.

Five cc. of 3% H_2O_2 solution was added and then each of the samples was boiled in a nickel crucible for ten minutes to destroy the excess H_2O_2 which remained after the oxidation of the sample. Incomplete destruction of the H_2O_2 resulted in the formation of a yellow complex when the molybdate solution was added. It was easy to mistake the yellow complex, just mentioned, for the yellow complex silicon formed with molybdate. It was found that boiling for ten minutes accompanied by washing the sides was sufficient to assure complete destruction of the H_2O_2.

After the solutions had cooled to room temperature their pH was adjusted to 1.5-1.7 with 9N sulfuric acid. The pH was determined by means of a pH meter (E40). In order to form the yellow complex color 5 cc. of acidified ammonium molybdate solution was added and the solution was allowed to stand for exactly 5 minutes.

Strickland (35) indicates that the molybdate solution should have from three to five equivalent of hydrogen ion per mole of molybdate. With this in mind, the molybdate solution was prepared by dissolving 25 grams of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ with 15.7 cc. of concentrated sulfuric acid and enough water to make 250 cc. Strickland indicated that the presence of the acid controlled which one of the two possible yellow complexes would be formed with the silicon.

Since the blue color of the silicon-molybdate complex was far more sensitive, it was used for the colorimetric determination of the silicon. It was developed five minutes after the addition of the molybdate by the addition of 10 cc. of 9N sulfuric acid, 10 cc. of 4% oxalic acid, and 10 cc. of 2.5% solution of $Fe(NH_4)_2(SO_4)_2$. The $Fe(NH_4)_2(SO_4)_2$ solution was prepared by dissolving the necessary amount of $Fe(NH_4)_2(SO_4)_2$ in 0.4 N sulfuric acid. The intensity of the blue color was measured 10 minutes after the reagents had been added. A colorimeter (E41) equipped with an 820 mμ interference filter (E42) was used to measure the intensity.

The use of Na_2CO_3 was most satisfactory in the above analysis; however, all commercial $NaCO_3$ has small amounts of silica as an impurity. The silica impurity is not appreciable until one attempts to analyze for 50 microgram quantities in which the procedure requires the use of 3 grams of Na_2CO_3. Most commercial sources supply reagent grade Na_2CO_3 with 0.005% silica. This is the equivalent of 150 micrograms of silica in three grams. By actual testing of the various lots from various manufacturers, a lot of sufficiently nearly pure with respect to silicon was found (E43). Ironically it turned out to be some material that was labeled "Calcined-Dry-Purified" in contrast with the best grade which is labeled "Analytical Reagent".

Since the silicon used for the preparation of the samples was known to be of high purity, it was used as a primary standard for the preparation of the calibration curve. A plot of the calibration curve appears in Figure 9. The least squares equation for this line was

$$\log_{10} \frac{I_o}{I} = 0.03605 \pm 0.00112 + 0.001425 \pm 0.000013 \mu g \text{ Si} \qquad (36)$$

The probable error in the weight of the material as determined from the above calibration curve was calculated to be 0.715%.

It was interesting to note that a rough estimate of the weight of silicon on the target could be made by observing the color of the target. The color of the target was observed to change from silver, to yellow, to red, to blue, to grey. The deep blue corresponds to about 80 μg of silicon on the target.

L. Boron Analysis

A coulometric method similar to that of Gilles, Iwamoto, Leitnaker, and Robson (36) was used for the analysis of boron. The method consisted of the internal generation of hydroxyl ions at the platinum cathode. The hydroxyl ions neutralized the acidic complex which was formed between boric acid and manitol. In order to prevent the generation of hydrogen ions at the anode, the anode was constructed of silver. A large excess of chloride ions

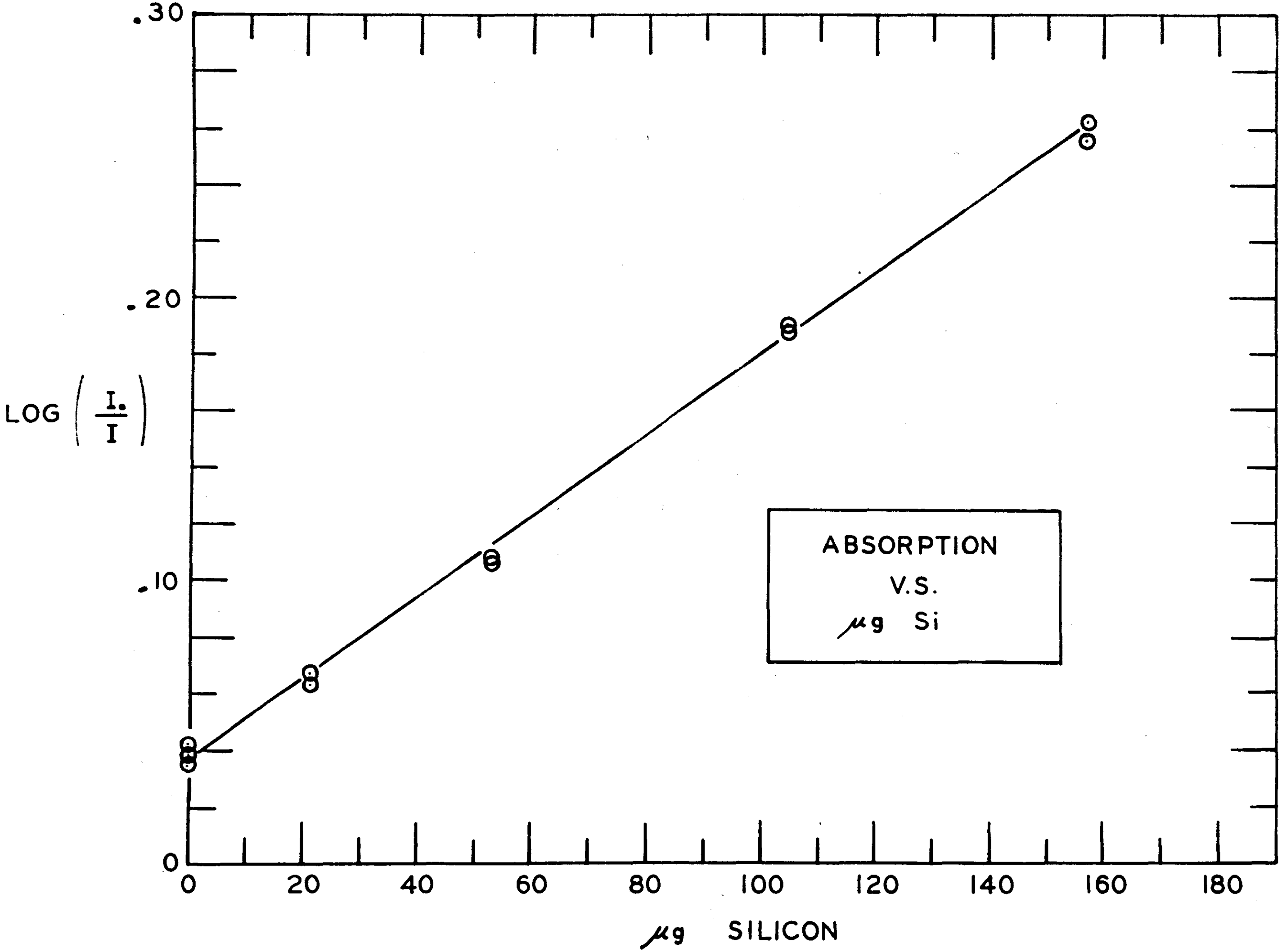

.30
.20
.10
0
LOG $\left(\frac{I_0}{I}\right)$
0
20
40
60
80
100
120
140
160
180
μg SILICON
ABSORPTION
V.S.
μg Si

FIGURE 9

was present in the solution, therefore AgCl was formed at the anode.

An exposed target from the SiB_6 vapor pressure measurements was analyzed by means of a spark spectrograph. The ratio of silicon to boron was found to be 100:1, therefore there was no need to analyze the targets for quantity of boron which had condensed on them.

The samples from the phase studies were analyzed for their boron content. A sample of about ten milligrams was fused with about two grams of Na_2CO_3 for thirty minutes at the full heat of a meeker burner. The fused sample was dissolved in water and diluted to 250 cc. volumetrically. A 5 cc. aliquot was used for the analysis.

In order to remove the dissolved carbon dioxide from the aliquot, the aliquot's pH was adjusted to 3 by the addition of dilute HCl and the solution was bubbled with oxygen free nitrogen for thirty minutes. The removal of the strong acid before the titration of the boric acid was accomplished by passing a current of five milliampers for about 100 seconds until the pH was 7.0. The complex between the manitol and the boric acid was then formed by the addition of 5 cc. of saturated manitol solution. This addition caused the pH to decrease to about 4.

The titration was carried out by passing a current of five milliampers through the solution. The current was precisely measured by noting the potential drop across a precision 10 ohm resistor (E44) with a potentiometer (E45). The end point for the titration was detected graphically as the time at which the greatest change in pH occurred. This occurred at about a pH of 8. The pH was measured by means of a commercial pH meter (E46). A clock (E47) was connected to measure the time during which current was passing through the electrolysis cell.

Gilles, et al., reported the need for making a correction for the blank. They attributed this to oxygen which had been adsorbed on the walls of the glass container for the electrolysis cell. It was found that a teflon beaker eliminated the need for a correction.

A test was made with the use of boric acid (E48) to determine the accuracy that could be obtained. The boric acid was fused with the Na_2CO_3, since the samples were also fused in this manner. It was found possible to obtain an accuracy of ±0.7%. An analysis by this method made on the boron used for the sample preparations (E14), showed it to be 97% boron.

V RESULTS

In this chapter a description will be given of the temperature-composition phase diagram for the silicon-boron system and of the pressure-composition diagrams at 1200, 1700, and 1900°C. for the silicon-boron system. The results of the measurements of the vapor pressure of SiB_6 will be presented. Finally, the thermodynamic properties for SiB_6 which were calculated from the vapor pressure measurements will be given.

A. Tempreature-Composition Phase Diagram

In order to describe the temperature-composition phase diagram for the silicon boron system, this section will contain a report of the preparation of the crystalline form of boron from amorphous boron, proof of the solid solution of silicon in boron, evidence for the existence of SiB_6 and SiB_3, and a demonstration of the solid solubility of boron in silicon. The temperature for the incongruent melting of SiB_6 and the temperature of the decomposition of SiB_3 will be indicated. Finally the distances and the intensities of the X-ray diffraction lines will be given.

There are three forms of crystalline boron. McCarty, Horn, Decker, and Newkirk (37) have reported a rhombohedral form with $a_o = 5.06$ Å and $\alpha = 58^\circ 4'$ with 12 atoms per unit cell. Hoard, Hughes, and Sands (38) reported a tetragonal form with $a_o = 8.473$ and $c_o = 5.030$ Å with 50 atoms per unit cell. Finally Sands and Hoard (39) presented evidence for a second rhombohedral form with $a_o = 10.12$ Å and $\alpha = 65^\circ 28'$ with 108 atoms per unit cell. When amorphous boron was heated in a ZrB_2 crucible to a temperature of 1753°C it was found to arrange itself according to the crystal structure with 108 atoms per unit cell.

Consider now the extent of the solid solubility of silicon in boron. Figure 10 is a plot of the lines which appeared on the X-ray diffraction films. The angle of the lines are plotted as a function of the composition by analysis of the sample. The compositions represented extend from pure boron to Si:6B. The identification numbers used were those from the X-ray diffraction log book number.

An examination of Figure 10 will reveal a gradual shift of the distances associated with the 108 atom per unit cell boron structure as the ratio of the silicon to boron increases. Film C-1425 is the first film in which lines could be detected which were associated with a second phase. Since the ratio of the material from which this film was prepared was Si:15.1B, it was concluded that the solubility of silicon in boron occurs from boron to the approximate ratio of Si:16B. The samples used for Figure 10 had been heated to temperatures between 1600 and 1800°C. A sample of Si:12B was heated at 1227°C. and the X-ray

X- RAY DIFFRACTION LINES VS. COMPOSITION

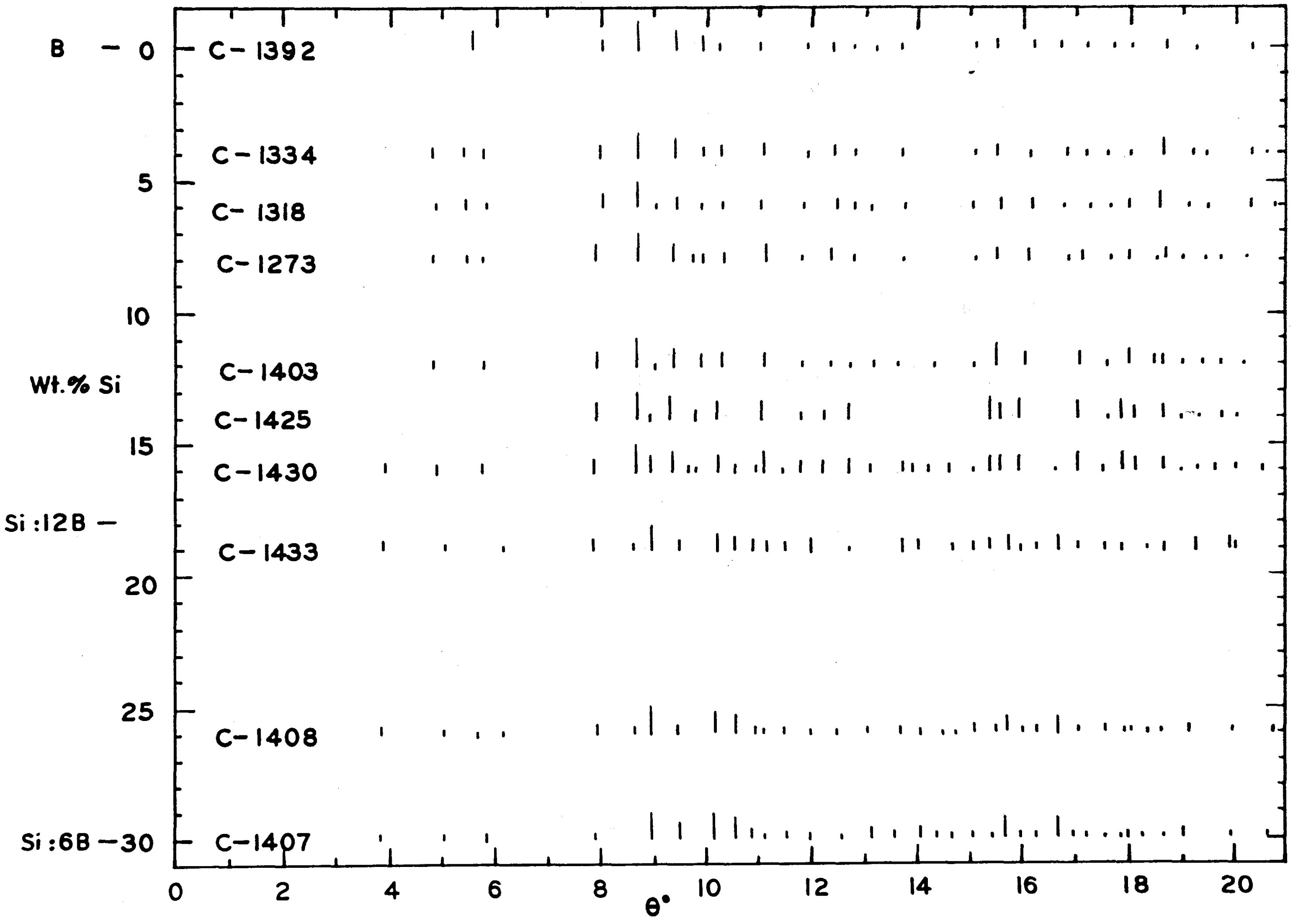


FIGURE 10

diffraction prepared from it indicated the presence of only one phase, the solid solubility of silicon and boron.

The lines of the second phase which appeared in Figure 10 were found to correspond closely with those reported by Cline (11) for SiB_6. Table VI gives a comparison between the diffraction pattern reported by Cline and the one found in this laboratory.

TABLE VI

X-RAY DIFFRACTION DATA FOR SiB_6

Cline (11)		This Laboratory (C-1407)	
"d" Å	Intensity	"d" Å	Intensity
11.47	20	11.35	20
9.12	10	8.68	10
7.62	20	7.47	5
5.57	10	5.57	10
4.92	100	4.94	100
4.62	40	4.64	40
4.35	70	4.35	90
4.23	80	4.19	80
4.15	50	4.08	20
3.99	20	3.98	10
3.86	40	3.85	20
3.70	30	3.71	20
3.53	10	3.54	10
3.45	30		
3.39	30	3.39	40
3.25	40	3.26	20
3.18	30	3.18	20
3.10	20	3.11	5
3.05	20	3.03	10
2.98	30	2.96	10
2.93	30	2.91	10
2.85	80	2.85	70
2.74	50	2.79	10
2.71	60	2.75	10
2.67	60	2.68	60

The variation between the two sets of diffraction data reported in Table VI was attributed to have occurred because the two samples may have been prepared at different temperatures. The lines arising from samples of SiB_6 which were known to have been prepared at different temperatures demonstrated some variation of their positions and intensities. The variation of the lines was not interpreted as evidence of a homogeneity range for SiB_6, since all of the X-ray diffraction patterns for SiB_6 showed either a phase richer or poorer in boron to be present also.

A new phase was found which had not been reported in the literature at the time this thesis was written. The new phase and SiB_6 appeared in samples with stoichiometry more rich in silicon than Si:3B. Silicon was absent from a sample, C-1507, which had the composition Si:3.5 and had been heated for twelve hours. The silicon phase was observed to be present in a sample, C-1511, with the composition Si:2.75B which had been heated for eighteen hours. On the basis of the above evidence it was concluded that the new compound was SiB_3.

Table VII presents the calculated diffraction pattern on the basis of Cline's unit cell for SiB_3 (8). Also in Table VII will be found the diffraction pattern which was found in this laboratory for SiB_3. The Miller indices which appear in the table were estimated for the "d" values by the use of Bunn charts (40). From the Bunn charts the SiB_3 found in this laboratory was characterized with a hexagonal unit cell with $a_o = 6.97$ and $c_o = 12.24$ Å. The lines recorded in Table VII were from X-ray diffraction pattern C-1511.

TABLE VII

X-RAY DIFFRACTION DATA FOR SiB_3

Cline (7)		This Laboratory (C-1511)		
"d" (Å)	hkl	"d" (Å)	intensity	hkl
		5.06	8	101
4.18	003	4.15	41	003
		3.16	24	111
		2.76	60	200
		2.68	100	104
2.46	012	2.51	5	113
		2.31	6	203
2.09	006	2.12	2	210
2.04	104	2.04	11	006
1.83	015	1.88	2	213
		1.76	10	007
		1.67	6	107
		1.606	22	220
1.55	101	1.582	10	221

Evidence was found for the solid solution of boron in silicon. The evidence was in the form of a decrease in the unit cell dimensions for silicon. A value of $a_o = 5.4308 \pm 0.0002$ Å for pure silicon, C-365, was calculated from a Hess least squares fit of the parameter to the indexed diffraction lines (41). The value for the parameter of the saturated solution was obtained from a sample of Si:6B which had been arc melted, C-1445. The value obtained for this sample for the parameter of the saturated solution of boron in silicon was $a_o = 5.4114 \pm 0.0002$ Å. The solubility limit of the boron in silicon is not known.

The phases have now been described. The results of experiments to demonstrate the incongruent melting of SiB_6 and the decomposition of SiB_3 will now be presented.

It was found that SiB_6 melted incongruently to form B (ss.) and a silicon-rich liquid when SiB_6 was heated above 1864 ± 6°C. Since the B (ss.) phase could have been formed by the preferential loss of silicon or by exceeding the incongruent melting point, the appearance the Si (ss.) phase in the X-ray diffraction patterns was used as the criterion for the incongruent melting. At a temperature of 1864°C. the silicon rich phase was liquid; however, upon cooling a portion of this phase became the Si (ss.) phase. It was found that when a sample of SiB_6 and B (ss.) was heated to 1858°C., C-1375, no Si (ss.) lines c ould be observed in the diffraction patterns. When a sample of the same composition was heated to 1870°C., C-1378, the cooled sample did show evidence for Si (ss.).

The phase SiB_3 was found to be unstable with respect to Si (ss.) and SiB_6 at temperatures above 1269 ± 10°C. Once again the appearance of Si (ss.) was used as the criterion of phase change. A sample composed of SiB_3 and

SiB_6 was heated to 1258°C. and there was no evidence of phase change, melting, or sintering, C-1519. When a sample of the same composition was heated to 1279°C., it gave evidence for the presence of Si (ss.). The sample did not appear to have been melted or to have been sintered in the last mentioned heating. Sintering of the samples did not appear to have occurred until after samples with the same composition had been heated to temperatures above 1306°C. It was concluded that the decomposition was a solid-solid process as contrasted with an incongruent melting process.

All of the above compounds appeared to be black in color. The above compounds were found to be very hard, since they were found to be capable of scratching agate. They were not found to be capable of scratching B_4C. All of the above compounds were found to be insoluble in oxidizing acids. This was assumed to be caused by the formation of an impervious coating of SiO_2. The compounds could be dissolved in a mixture of HF and HNO_3 acids. The compounds paralleled silicon in their ability to be dissolved in NaOH solution. No difficulty was found in fusing the compounds with melted Na_2CO_3.

Now that the compounds found in this laboratory have been presented a discussion of the work of others on the silicon boron system will be presented. Neither Brewer, et al. (3) nor Stavrolakis, et al. (4) were able to find any compound formation between silicon and boron. The temperatures of their experiments were sufficiently low if the value they report is correct. They may have been searching for compounds with much more simple diffraction patterns than that of SiB_6. If their X-ray diffraction patterns were not exposed sufficiently long, they could have readily mistaken the lines of SiB_6 for those of boron.

The work of Samsonov and Latysheva (5) on SiB_3 has already been questioned in their own country and they have not supported their claims. Adamsky (12) was also unable to duplicate their work. The compound they reported may have had a composition that included elements other than silicon and boron.

There is some uncertainty about the compound reported by Rizzo (7), since at the time of his report he had not obtained a report of the analysis of his material. There is the possibility that his compound may have been some compound other than SiB_3 or SiB_4.

There are some similarities between the SiB_3 found in this laboratory and the SiB_3 reported by Cline (7). The c_0 parameter of the two compounds are almost identical and the compound found in this laboratory has an a_0 value of almost twice that of Cline's compound. Cline determined his unit cell from single crystal X-ray diffraction patterns. Single crystals were not obtained in this laboratory. It may be that one of the two compounds is a metastable form and that the unit cell that one obtains is governed by the method of preparation.

The crystal structure reported by Zhuravlev (9) for the compound prepared by Samsonov and Markovski (8) which was said to be SiB_6 is questioned. It was believed at one time that this compound was prepared in this laboratory, but it was later found that the compound prepared was CaB_6. The compound CaO had been sublimed from a stabilized zirconia crucible into the sample. The unit cell parameters reported by Zhuravlev were practically the same as the accepted values for CaB_6.

The compound reported by Parthe (14) to be SiB_{12} may be incorrect. There is the possibility that this compound is stable at a temperature which was not investigated in the course of this research. It is also possible that Parthe's compound may have represented a point in the boron solid solution.

It is possible that still other compounds may be found to be stable at temperatures which were not investigated in the course of this research.

Figure 11 is the temperature-composition phase diagram which was deduced for the silicon boron system. Each of the points on the phase diagram correspond to one of the heatings represented in Table VIII. The composition of the points

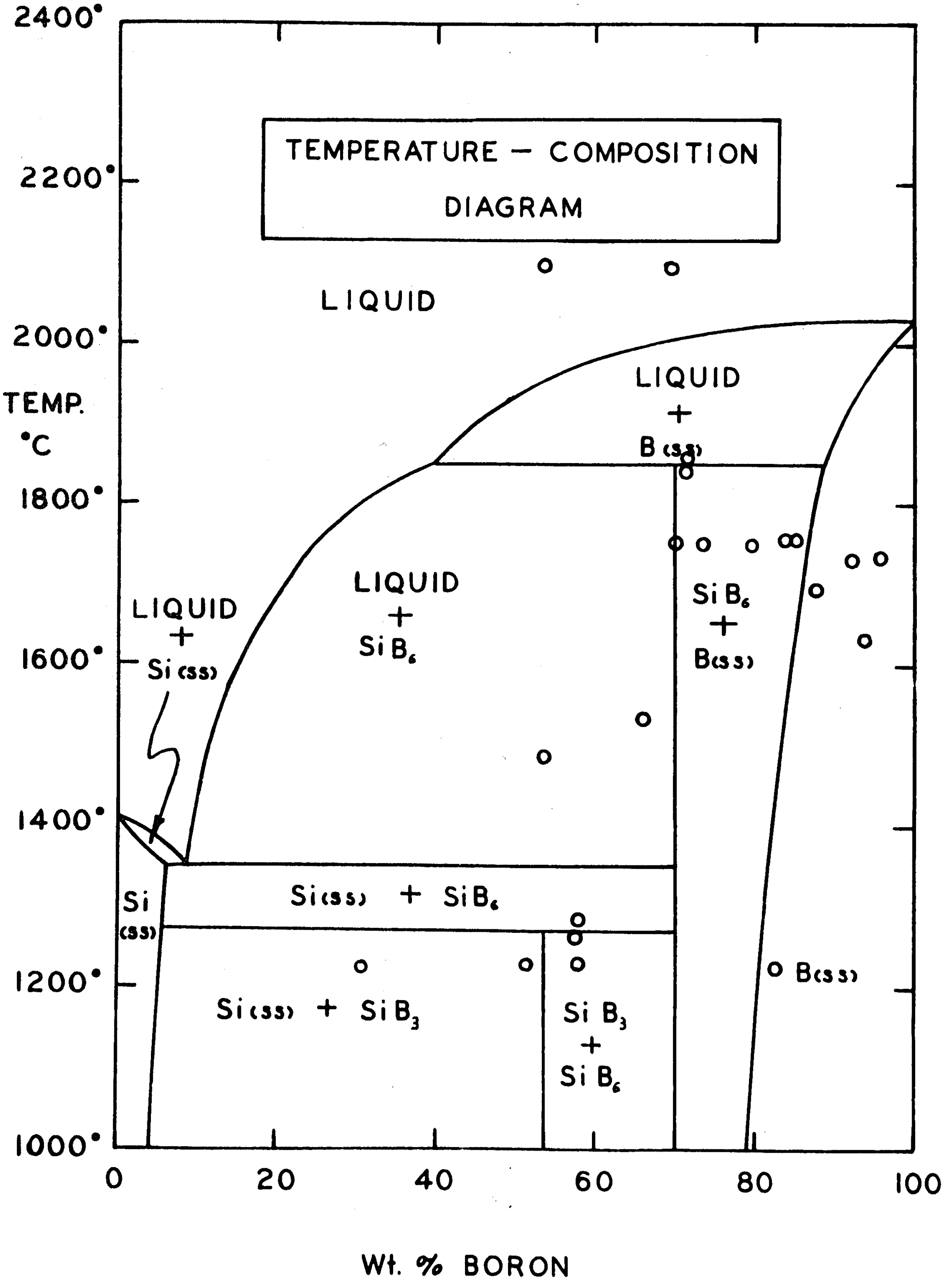

TEMPERATURE – COMPOSITION DIAGRAM
2400°
2200°
2000°
1800°
1600°
1400°
1200°
1000°
TEMP. °C
LIQUID
LIQUID + B(ss)
LIQUID + SiB6
LIQUID + Si(ss)
SiB6 + B(ss)
Si(ss) + SiB6
Si (ss)
Si(ss) + SiB3
SiB3 + SiB6
B(ss)
0
20
40
60
80
100
Wt. % BORON

FIGURE 11

represented in Table VIII were determined by one of two methods. At the lower temperatures it was found that the samples lost less than one percent upon being heated; therefore, the composition of these samples was determined by synthesis. At the temperatures above 1550° it was found that samples usually lost significant amounts of silicon, therefore the composition of these samples was determined by the analysis of the silicon by the colorimetric method already described. The composition of the samples in Table VIII have been expressed by two methods for the convenience of the reader.

TABLE VIII

HEATINGS PERTINENT TO PHASE DIAGRAMS

Identification	Composition		Phases Present	Temp. deg. C.
	At. Ratio B to Si	% B		
C -365	0.0	00.0	Si	Mfg.
C-1531	1.5	31.4	Si(ss), SiB_3	1227
C-1511	2.7	51.4	Si(ss), SiB_3	1227
D- 629	3.0	53.6	Si(ss), SiB_6	1490
C- 645	3.0	53.6	Si(ss), B(ss)	arc melt
C-1507	3.5	57.4	SiB_3, SiB_6	1227
C-1519	3.5	57.4	SiB_3, SiB_6	1258
C-1520	3.5	57.4	Si(ss), SiB_3, SiB_6	1279
C-1525	5.0	65.8	Si(ss), SiB_6	1535
C-1445	6.0	69.8	Si(ss), B(ss)	arc melt
C-1444	6.2	70.5	SiB_6, B(ss)	1763
C-1375	6.5	71.4	SiB_6, B(ss)	1858
C-1378	6.5	71.4	Si(ss, SiB_6, B(ss)	1870
C-1408	7.4	74.0	SiB_6, B(ss)	1763
C-1433	10.7	80.5	SiB_6, B(ss)	1763
C-1430	14.3	84.6	SiB_6, B(ss)	1863
C-1425	15.1	85.4	SiB_6, B(ss)	1763
C-1403	18.3	87.6	B(ss)	1709
C-1273	31.2	92.3	B(ss)	1648
C-1318	38.7	93.7	B(ss)	1753
C-1334	60.7	95.9	B(ss)	1753
C-1392	inf.	100.0	B	1753

B. Pressure-Composition Phase Diagrams

The temperature-composition diagram has been presented. The pressure-composition diagrams for temperatures of 1200, 1700, and 1900°C. will now be discussed. Two forms of evidence were used to determine the nature of the vapor phase, an analysis of the condensed phase after vaporization had occurred and analysis of the vapor which had been condensed on the platinum targets.

Table IX presents the results of the analysis of the composition of samples before and after a portion of them had been vaporized. The note book page was used for identification purposes. Since in all cases the samples changed composition, it is apparent that neither SiB_6 nor B (ss.) show any tendency for congruent vaporization. It is also apparent that both SiB_6 and B (ss.) preferentially vaporize silicon. The final phases of 772 were interpreted as evidence for the slow diffusion of silicon through the sample.

TABLE IX

COMPOSITION CHANGES FROM VAPORIZATION

Iden.	Temp. deg. C.	Initial Ratio B/Si	Initial Phases	Final Ratio B/Si	Final Phases
782	1753	6.14	SiB_6, B(ss.)	7.42	SiB_6, B(ss.)
772	1700	7.98	SiB_6, B(ss.)	18.3	SiB_6, B(ss.)
691	1700	15.8	B(ss.)	28.7	B(ss.)
692	1743	60.7	B(ss.)	67.5	B(ss.)

Vapor from the vaporization of SiB_6 was collected on a platinum target by the use of the effusion apparatus. An emission spectrographic analysis of the material on the target indicated the ratio of Si:B on the target to be 100:1. This result was interpreted to indicate that silicon was the only species vaporized from SiB_6.

No vapor studies were made for SiB_3. Since SiB_3 was even more rich in silicon than SiB_6 and SiB_6 was found to vaporize silicon preferentially, it was concluded that SiB_3 would also vaporize silicon preferentially.

In order to give more than qualitative pressure-composition diagrams the pressures of silicon and boron represented in the diagrams are those found in the literature (42). The values for SiB_6 are the values which were found as a result of this research. A more detailed report of the vapor pressure of SiB_6 will be given in the section which follows. Table X gives the values which were used to prepare the three pressure-composition diagrams.

TABLE X

PRESSURE-COMPOSITION DIAGRAM DATA

Temperature	Log Vapor Pressure		
	Silicon	SiB_6	Boron
1900°C.	-3.75	-5.01	- 6.36
1700	-4.23	-5.01	- 7.85
1200	-7.91	-9.54	-13.09

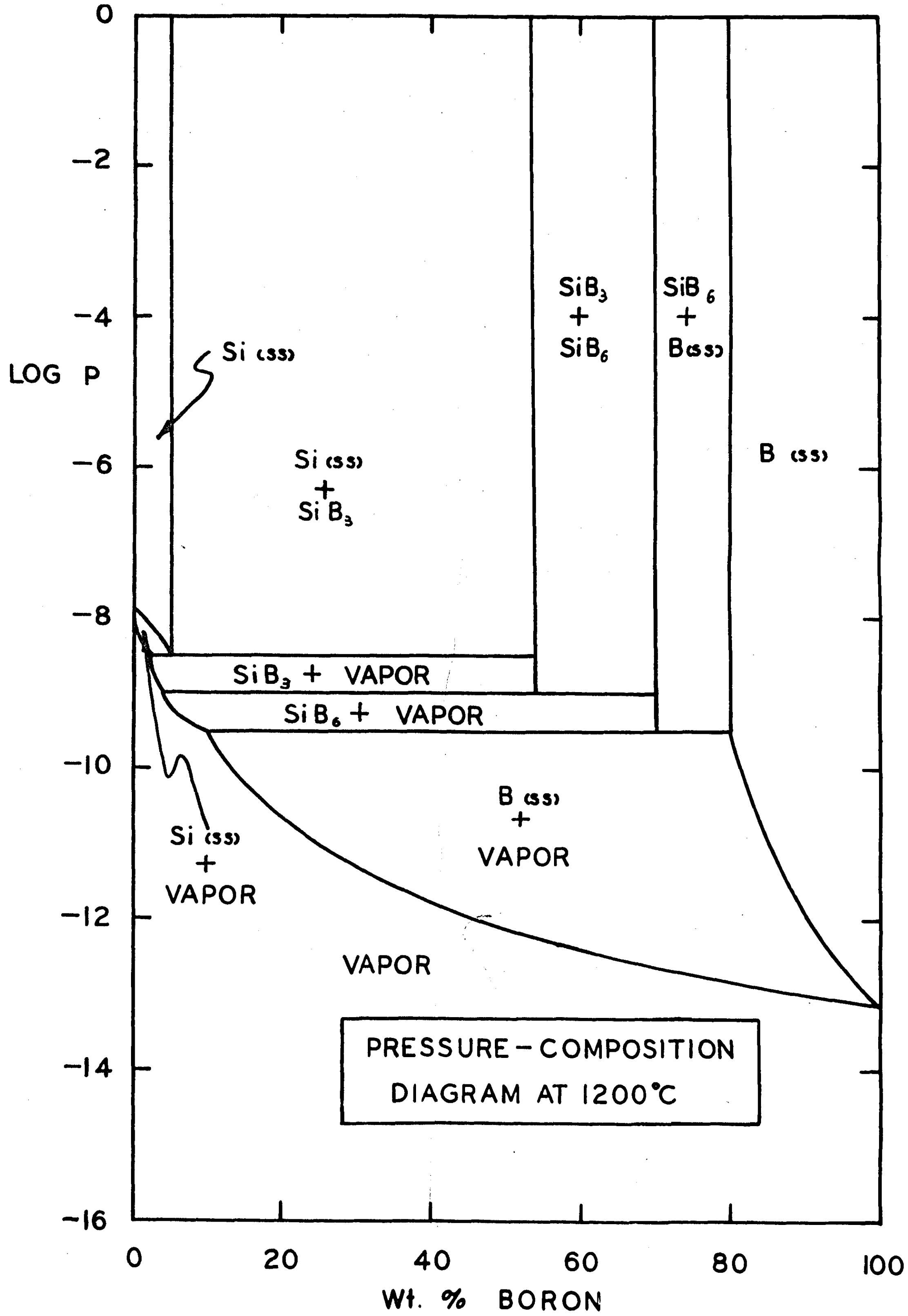
Figures 12, 13, and 14 depict the pressure-composition phase diagrams for temperatures of 1200, 1700, and 1900°C.

C. Measurement of the Vapor Pressure of SiB_6

Since the nature of the vapor species for SiB_6 has been presented, in this section the results of the vapor pressure measurements will be given. Before the results are presented, proof will be given to show that the vapor pressure of SiB_6 was constant when the two condensed phases SiB_6 and B (ss.) were present. In addition, three forms of proof will be offered to indicate that all of the vapor which impinged upon the platinum target was condensed.

In order to demonstrate the constancy of the pressure of SiB_6-B (ss.) at constant temperature, a series of five measurements of the vapor pressure were made, the sample was removed and returned to the crucible, and four more measurements of the vapor pressure were made. The results are shown in Figure 15 and in Table XIII. The sample was removed after the fifth measurement for analysis.

This experiment was very interesting, since it demonstrated a gradual decrease of the vapor pressure as the amount of silicon which had been vaporized increased. After the sample had been removed and returned to the crucible the vapor pressure returned to practically the same initial value and then the vapor pressure once again appeared to decrease, but much more slowly.



0
-2
-4
-6
-8
-10
-12
-14
-16
LOG P
Si (ss)
Si (ss) + Si B$_3$
SiB$_3$ + SiB$_6$
SiB$_6$ + B(ss)
B (ss)
SiB$_3$ + VAPOR
Si B$_6$ + VAPOR
B (ss) + VAPOR
Si (ss) + VAPOR
VAPOR
PRESSURE – COMPOSITION DIAGRAM AT 1200°C
0
20
40
60
80
100
Wt. % BORON

FIGURE 12

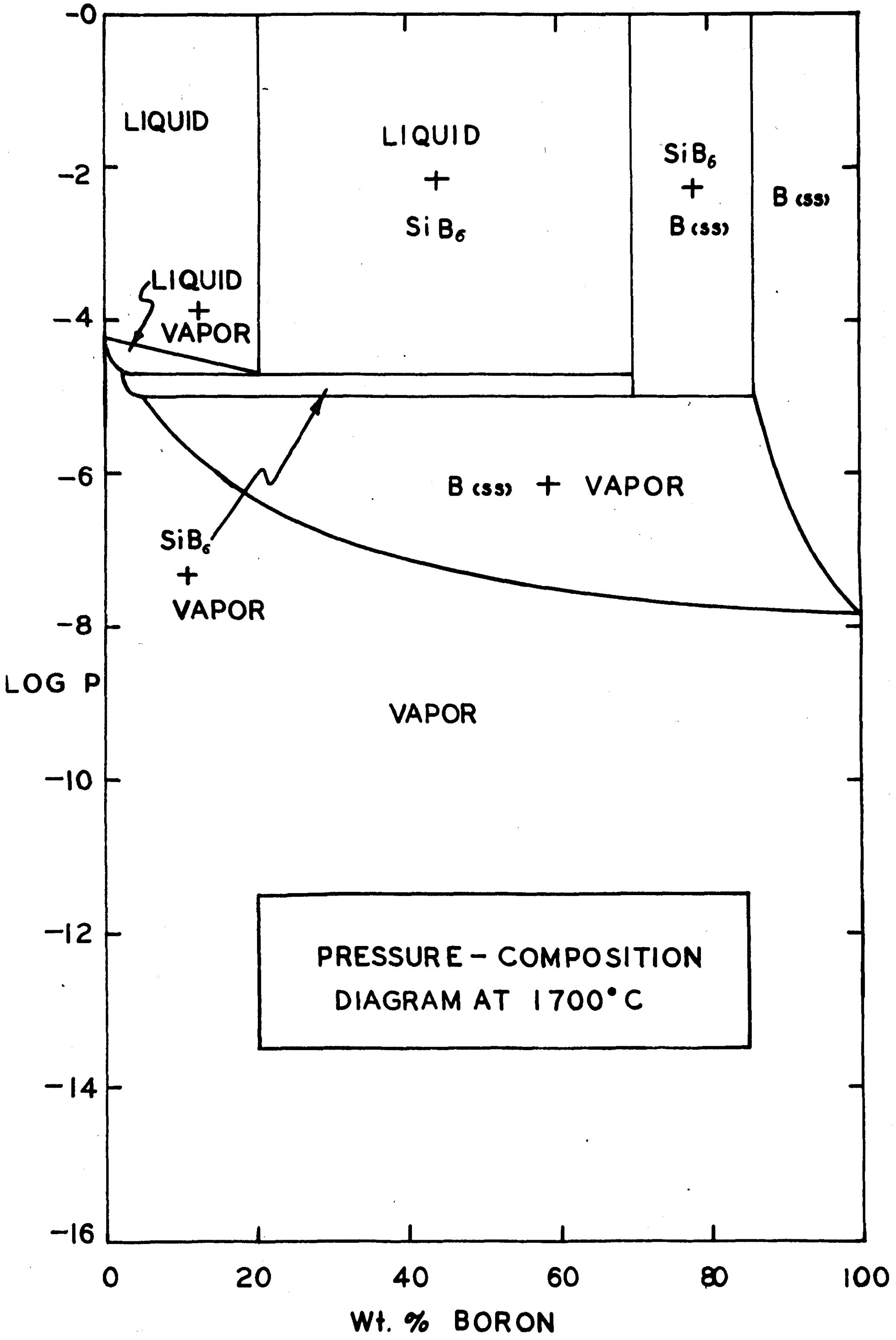

LIQUID
LIQUID + SiB$_6$
SiB$_6$ + B(ss)
B(ss)
LIQUID + VAPOR
B(ss) + VAPOR
SiB$_6$ + VAPOR
VAPOR
LOG P
-0
-2
-4
-6
-8
-10
-12
-14
-16
0
20
40
60
80
100
Wt. % BORON
PRESSURE – COMPOSITION DIAGRAM AT 1700° C

FIGURE 13

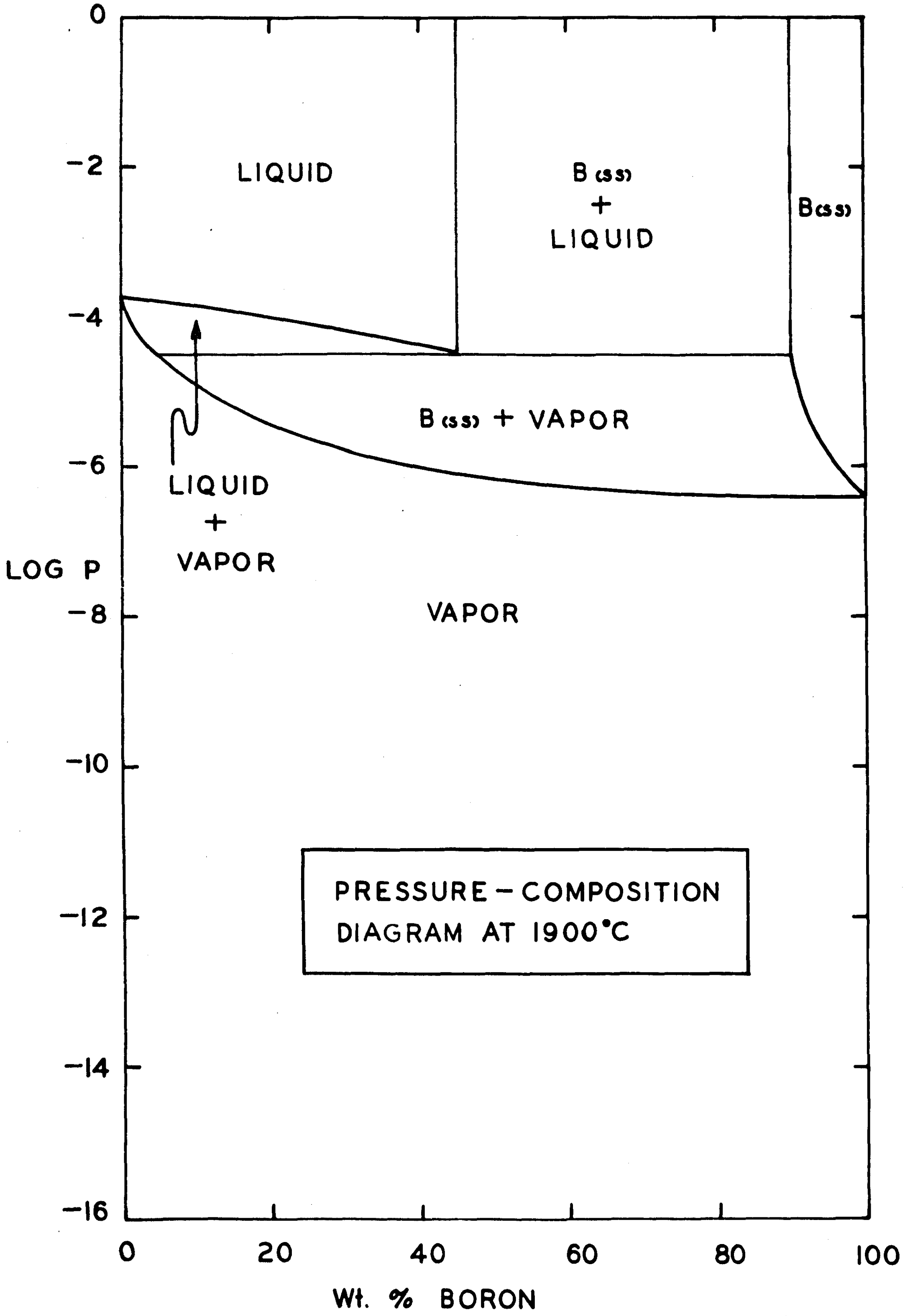
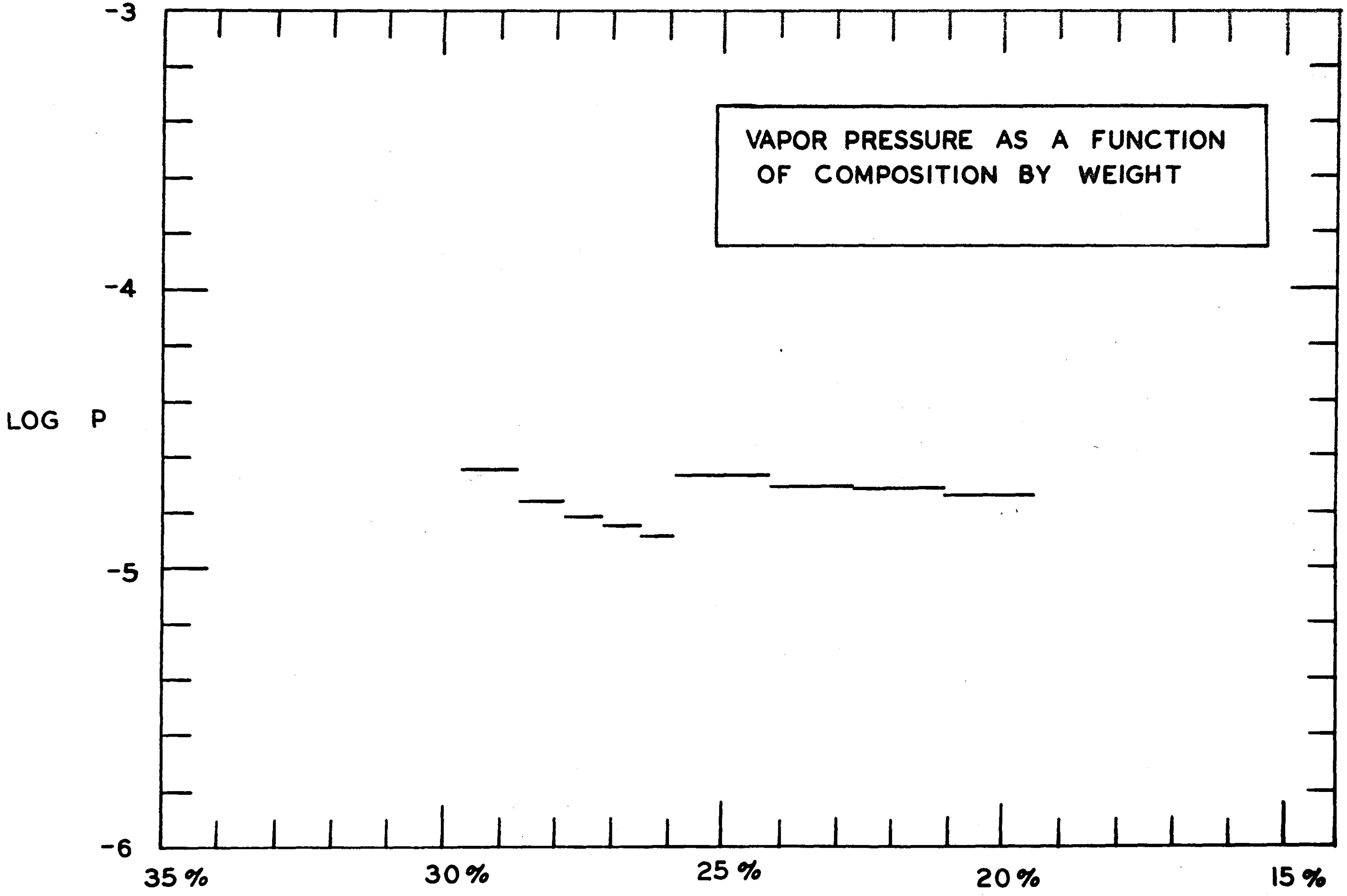

0
-2
-4
-6
-8
-10
-12
-14
-16
LOG P
LIQUID
B (ss) + LIQUID
B(ss)
B (ss) + VAPOR
LIQUID + VAPOR
VAPOR
PRESSURE – COMPOSITION DIAGRAM AT 1900°C
0
20
40
60
80
100
Wt. % BORON

FIGURE 14


-3
-4
-5
-6
LOG P
VAPOR PRESSURE AS A FUNCTION OF COMPOSITION BY WEIGHT
35 %
30 %
25 %
20 %
15 %

% Si FIGURE 15

The vapor pressure was accepted to be constant, since repacking the sample in the crucible increased its calculated vapor pressure nearly to its initial value. The decrease of the apparent vapor pressure with the amount vaporized for a given packing of the sample was attributed to the slow diffusion of silicon through the sample. It was not attributed to the amount of silicon available for vaporization because the vapor pressure increased after the sample had been repacked.

It is interesting to add that the first time the sample was placed in the crucible it was packed more tightly than the second time. The effect of diffusion was much more pronounced in the first series, since the sample was packed more tightly.

Three forms of proof will now be presented to show that all of the silicon which impinged upon the targets was condensed. The first form of evidence was the shadow cast by the defining ring of the magazine. If the edges of the shadow gradually faded, one might have concluded that not all of the vapor had been condensed. The indistinct target shadow would have been caused by the failure of some silicon atoms to stick the first time, their being deflected to the top surface of the collimating ring, their being deflected again to the target, and finally being condensed. The shadow cast was sharp; therefore, there was no evidence for the bouncing just described.

The temperature of the targets was measured as a function of the temperature of the effusion cell. This was done to determine if the targets remained sufficiently cool during the condensation of the vapor to assure that all of the silicon was condensed. This was accomplished by spot welding a thermocouple to the platinum target. Table XI presents the results from this measurement. From the temperatures of the targets measured there was no reason to suspect that part of the silicon vapor was not condensed.

TABLE XI

TARGET TEMPERATURES VS. EFFUSION CELL TEMPERATURES

Temperature of Cell	Temperature of Target
1435°C.	219°C
1542	261
1647	310
1748	357
1807	400

It was assumed that the fraction of the vapor striking the target which was restituted to the vapor was a function of the quantity of silicon which had already been deposited on the target. If this were true and not all of the silicon was condensed on the target, the vapor pressure measured would decrease with increasing length of exposure of the target. Table XII demonstrates that there was no trend in the data which corresponded to the length of exposure of the target. The third experiment, therefore, supported the conclusion that all of the silicon vapor which struck the platinum target was condensed.

TABLE XII

VAPOR PRESSURE OF SiB_6 VS. TIME OF VAPOR COLLECTION

Identification	Time Duration	Logarithm of Pressure Measured
791-10	40.0 min.	-4.721
791-12	20.0	-4.708
791-15	10.0	-4.682
791-16	20.0	-4.759

Table XIII and XIV give the data which were used to calculate the vapor pressure of SiB_6. Table XV gives the composition of the sample before and after vaporization for a series. The values preceded by ca. were calculated from the fraction of the sample vaporized. The other compositions were established by wet analysis of the silicon content. Table XVI gives the pressures which were calculated and the data which were used to prepare Figure 16, a plot of the vapor pressure of SiB_6 as a function of the absolute temperature.

D. Thermodynamic Quantities for the SiB_6 Vaporization

Now that the vapor pressure of SiB_6 from 1489 to 1807°C. has been presented, the thermodynamic quantities that were calculated for the vaporization of SiB_6 will be

TABLE XIII

VAPORIZATION DATA

Iden.	Area of Orifice mm.	Time sec.	Temp. °K	Weight Si μg Target
71309	7.64	2700	1976	85
71312	7.64	7213	1866	33.0
71809	7.64	2713	1921	37.5
71810	7.64	628.8	2029	36.0
71812	7.64	14405	1811	31.5
74510	1.80	1800	2092	70.0
74512	1.80	2400	2092	76.0
74515	1.80	3000	2036	47.0
74516	1.80	4502	1982	40.5
75509	1.80	898	2090	46.0
75510	1.80	2402	2036	58.5
75512	1.80	4291	1982	52.0
76209	7.64	1200	2036	70.5
76210	7.64	7200	1926	69.0
76212	7.64	12600	1871	53.5
76215	7.64	28804	1762	25.0
76709	7.64	3600	1982	101.5
76710	7.64	28800	1815	56.0
76712	7.64	1200	2038	53.0
76715	7.64	3600	1982	67.0
76716	7.64	14414	1870	48.0
78209	7.64	1200	2037	75.5
78210	7.64	1200	2037	57.0
78212	7.64	1200	2037	51.0
78215	7.64	1200	2037	46.0
78216	7.64	1200	2037	42.5
78409	7.64	1200	2037	71.0
78410	7.64	1200	2037	64.0
78412	7.64	1200	2037	63.0
78415	7.64	1200	2037	59.0
79110	7.64	2400	2037	126
79112	7.64	1200	2037	65
79115	7.64	600	2037	34.5
79116	7.64	1204	2037	58

TABLE XIV

DATA FOR GEOMETRY FACTOR

Identification	r cm.	l cm.	R cm.	L cm.	Fraction Collected x10^{-3}
713	0.1562	0.508	1.193	13.91	6.91
718	0.1562	0.508	1.193	13.91	6.91
745	0.0758	0.450	1.193	14.01	6.44
755	0.0758	0.450	1.193	14.01	6.44
762	0.1562	0.508	1.193	14.03	6.81
767	0.1562	0.508	1.193	14.03	6.81
782	0.1562	0.508	1.193	14.03	6.81
784	0.1562	0.508	1.193	14.03	6.81
791	0.1562	0.508	1.193	14.03	6.81

TABLE XV

COMPOSITION OF VAPORIZATION SAMPLE

Iden.	% Sample Vaporized	% Silicon Initially	% Silicon Finally	% Available Silicon Remaining
713	9.2	ca. 25.7	ca. 18.2	32.6
718	7.8	ca. 28.6	ca. 22.5	53.5
745	9.8	ca. 28.6	ca. 20.8	42.2
755	7.7	ca. 28.6	ca. 22.6	57.3
762	5.9	ca. 28.6	ca. 24.1	65.3
767	8.8	ca. 29.2	ca. 22.4	50.8
782	6.1	29.7	25.9	72.3
784	4.5	25.9	19.4	42.0
791	6.2	ca. 29.7	ca. 25.1	66.5

TABLE XVI

VAPOR PRESSURE DATA

Iden.	Symbol	Pressure 10^{-7} atm.	log P	$10^4/T$
71309	○	112.5	-4.949	5.081
71312		15.89	-5.799	5.367
71809	△	48.70	-5.313	5.219
71810		207.3	-4.684	4.953
71812		7.482	-6.126	5.521
74510	●	650.2	-4.188	4.807
74512		529.5	-4.277	4.807
74515		258.4	-4.589	4.935
74516		146.4	-4.835	5.068
75509	■	855.9	-4.068	4.808
75510		401.8	-4.397	4.936
75512		197.2	-4.706	5.068
76209	□	212.6	-4.672	4.936
76210		33.76	-5.472	5.208
76212		147.5	-5.831	5.356
76215		2.929	-6.533	5.675
76709	▽	100.0	-4.997	5.068
76710		6.660	-6.716	5.510
76712		159.8	-4.796	4.936
76715		66.47	-5.177	5.068
76716		11.57	-5.937	5.356
78209	▯	227.7	-4.643	4.936
78210		171.9	-4.765	4.936
78212		153.8	-4.813	4.936
78215		138.7	-4.858	4.936
78216		128.2	-4.892	4.936
78409	▯	214.1	-4.669	4.936
78410		193.0	-4.714	4.936
78412		190.0	-4.721	4.936
78415		177.9	-4.749	4.936
79110	▯	190.0	-4.721	4.936
79112		190.6	-4.708	4.936
79115		208.1	-4.682	4.936
79116		174.3	-4.759	4.936

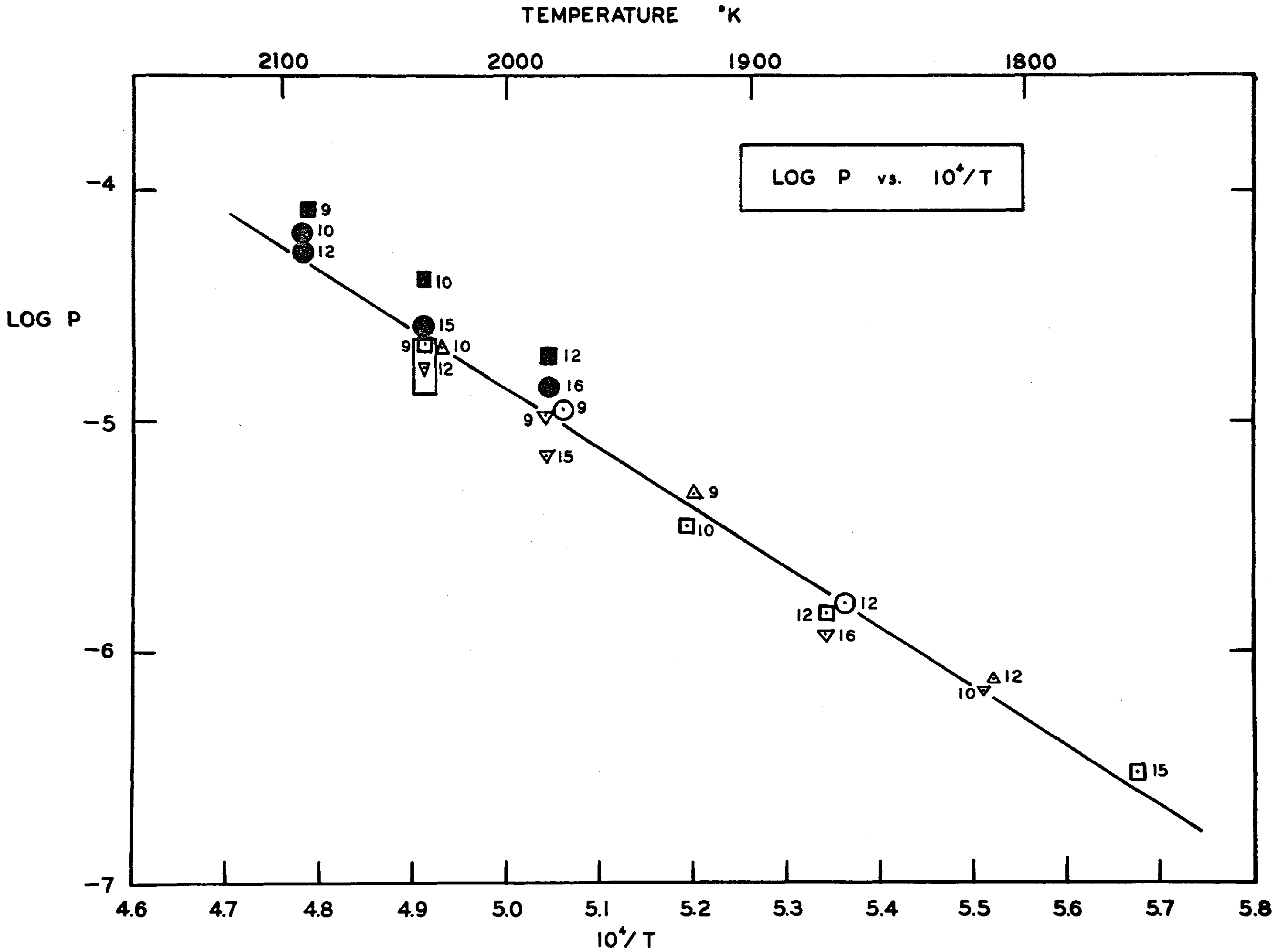

TEMPERATURE °K
2100
2000
1900
1800
LOG P vs. 10⁴/T
LOG P
−4
−5
−6
−7
4.6
4.7
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
5.6
5.7
5.8
10⁴/T
9
10
12
10
15
9
10
12
12
16
9
9
15
9
10
12
12
16
12
10
15

FIGURE 16

indicated. The methods given in the theoretical chapter were used to calculate the thermodynamic quantities.

The first method required the fit of a straight line to the logarithm of the pressures as a function of the reciprocal of the absolute temperature. This fit was accomplished by means of a least squares fit. Equation (37) presents the results of the least squares fit of Table XVI,

$$\log P = \frac{-26009 \pm 573}{T} + 8.142 \pm 0.289 \qquad (37)$$

In order to obtain a more nearly accurate value for the parameters of equation (37), some of the pressure measurements were disregarded and others were weighted more strongly. It was apparent from Figure 15 that there was a decrease in the pressure measured after the first effusion from the samples 782 and 784. For this reason only the first points of the two series were considered to be accurate; therefore the others were disregarded for the purposes of the least squares fit. It was considered possible for point 78209 to be high because of the presence of unreacted silicon in the sample. For this reason a mean value between 78209 and 78210 was selected and was weighted four times, since the knowledge of the other points contributed to the confidence of this mean value. Measurement 78409 was weighted three times for the same reason. There were probably other points more reliable than others, but these described above were the only pressures for which sufficient information was available to merit weighting.

From equation (37) a value of 119.02 ± 2.62 kcal/mole was calculated for the standard enthalpy for the process,

$$SiB_6\ (s) \rightarrow Si(g,\ 1\ atm) + 6B\ (s) \qquad (38)$$

If the assumption was made that the extent of the solubility of silicon in boron was Si:16B and that the activity of the boron was equal to its mole fraction in the solid solution, a value of 36.53 ± 1.29 e.u. was calculated for the standard entropy of the above process.

It was also possible to calculate a value for the enthalpy of the above process by the use of the third law method presented in the theoretical section. In order to use this method it was necessary to estimate a value for the entropy of the above process. The entropy was estimated from the estimated entropy of the decomposition of SiB_6 to form solid silicon and solid boron and the entropy for the vaporization of silicon.

The entropy associated with the dissociation of SiB_6 to give solid silicon and solid boron was estimated from the entropy for the decomposition of B_4C to give solid boron and solid carbon. B_4C was used, since silicon is directly below carbon in the periodic table. Another reason for the use of B_4C was that both B_4C and SiB_6 have similar crystal structures (12).

In B_4C three carbon atoms are arranged in a chain in the holes between the icosahedron formed of twelve boron atoms. In SiB_6 two silicon atoms are arranged in the holes between the icosahedron. The decomposition of B_4C results in the removal of three carbon atoms from twelve boron atoms. The decomposition of SiB_6 results in the removal of three silicon atoms from eighteen boron atoms. It was reasoned that the entropy for the decomposition of SiB_6 should be approximately 3/2 as much as for the decomposition of B_4C. The value for the decomposition of B_4C is 0.10 e.u., therefore the value for the entropy of the decomposition of SiB_6 should be approximately 0.15 e.u.

In order to estimate a value for the process represented in equation (38), it was necessary to estimate the entropy for the vaporization of silicon from the solid at 1900°K. The temperature of 1900°K was selected, since this was a representative temperature for the range over which the temperature measurements were made. Silicon melts at 1683°K. An entropy value was estimated for the sublimation process by making a plot for the entropy values at the lower temperatures (42) and extrapolating. This led to a value of 33.70 e.u. for the sublimation at 1900°K. A summation of the two values led to an estimation of 33.85 e.u. for the entropy of the process represented in equation (38) at 1900°K.

In order to calculate a third law heat of vaporization for each of the pressures which were measured, the entropy was assumed to remain constant over the temperature range for which the measurements were made. The third law heats are represented in Table XVII. These values led to a mean value for the heat of vaporization of 113.42 kcal/mole.

A combination of the heat capacity data for the reactants and the products (42, 43, 44) and the enthalpy calculated by the third law method at 1900°K. led to a value of 112 kcal/mole for the enthalpy of the process at 298°K. A similar calculation led to a value of 32.26 e.u. for the entropy of the process at 298°K. Since a measured value of the heat capacity of SiB_6 was not available, the heat capacity of SiB_6 was estimated to be equal to 7/5 that of B_4C.

A value of -7.00 kcal/mole was calculated for the enthalpy of formation of SiB_6 at 298°K. and a value of 1.33 e.u. was calculated for the entropy of formation at 298°K. In order to make these calculations it was necessary to employ the values for the enthalpy and entropy of vaporization of silicon (42).

A test was made to determine if the error estimated from the internal consistency was the same as that obtained from the external consistency. The probable error of each of the quantities of equation (36) was considered in order

TABLE XVII

THIRD LAW HEAT OF VAPORIZATION

Temp.	Identification	ΔH^{o} kcal/mole
2092	75509	110.49
2092	74510	110.90
2092	74512	112.64
2038	76712	113.84
2037	78209	113.16
2037	78210	114.33
2037	78212	114.78
2037	78215	115.21
2037	78216	115.42
2037	78409	113.41
2037	78410	113.84
2037	78412	113.91
2037	78415	114.17
2037	79110	113.90
2037	79112	113.78
2037	79115	113.54
2037	79116	114.27
2036	74515	112.60
2036	76209	113.39
2029	71810	113.10
1982	75512	110.69
1982	74516	111.89
1982	76709	113.39
1982	76715	114.68
1976	71309	112.60
1926	76210	114.46
1921	71809	112.74
1871	76212	114.33
1870	76716	115.20
1866	71312	113.31
1815	76710	113.39
1811	71812	113.17
1762	76215	113.46

to determine the internal consistency. They follow:

The probable error in the weight of material determined to have been collected on the target was found to be 0.71% for a typical point.

For the area of the larger orifice, the probable error was determined to 0.06%.

The time was estimated to be in error by ± 0.05 minutes. This is the equivalent of a probable error of 0.001% for the time of a typical exposure.

The error in the temperature was considered to be from two sources, the consistency with which the temperature could be maintained and the precision which could be obtained for measurements made with the optical pyrometer. The probable error calculated for the mean of the temperature measurements made during a typical exposure was considered to be a measure of both these quantities. This probable error was found to be 0.017%. This is less than the estimated error in the calibration of the optical pyrometer, therefore the error estimated by the National Bureau of Standards was used, 0.26%.

The error in the fraction collected was estimated to occur primarily in the integration by Freeman and Searcy. They estimated the error of their integration to be 1%, therefore this was the value used for the probable error of the fraction collected.

By the law of the propagation of errors this led to a value of 1.25% for the mean of the pressure measurements.

The probable error for the mean of the pressures represented in Figure 15 was found to be 7.19%. This value far exceeds the value estimated from the internal consistency. It thus appears that the largest source of error in the measurements of the vapor pressure of SiB_6 was the apparent slow diffusion of silicon through the sample.

It will be noted in Figure 16 that the pressures measured by the use of the smaller orifice were slightly higher than those measured with the larger orifice. It is possible that the smaller orifice improved the equilibrium conditions inside the crucible by the decrease in the effusion rate. It is also possible that the susceptor cover which was used with the smaller orifice was not properly designed and caused a higher fraction of the vapor to effuse in the direction of the target. It is not clear whether the points measured with the smaller orifice are more accurate or less accurate than those measured with the larger orifice.

An examination of the third law heats for the individual points reveals that the higher temperature values are as a whole lower than the low temperature values. This may or may not have been caused by low temperature measurements at the higher temperatures.

It was a pleasure to note that there was no evidence for any attack or wetting of the ZrB_2 crucible after all the pressure measurements had been made. From this it was concluded that there was no reason to suspect any changes had been made in the products of the SiB_6 vaporization as a result of interaction with the crucible.

VI SUMMARY OF RESULTS

This section will contain three parts. The first will contain a summary of the phases which were confirmed, the new phases that were found, some of their properties and the important aspects of the temperature-composition diagram. The second will contain the important aspects of the pressure-composition diagram. Finally, the last part will contain the enthalpy and entropy for the standard state vaporization and the enthalpy and entropy of formation of SiB_6.

A. Phases Prepared and Their Properties

Since the temperature-composition diagram has already been presented in Figure 11 only the important features of the diagram will be reported.

Silicon was found to form a solid solution in boron. The range of the solid solubility was found to extend to the ratio Si:16B at 1763°C. This extended homogeneity phase has not been reported in the literature.

A compound SiB_6 was prepared which confirmed the phase prepared by Cline (11), orthorhombic, $a_o = 14.39$, $b_o = 18.27$, and $c_o = 9.88$ Å. Cline stated that he found the material to melt at 1950°C.; however, it was found in this laboratory that the phase melted incongruently at 1864 ± 6°C.

A new phase SiB_3 was found which had a crystal structure different from those which had been reported for SiB_3. From X-ray diffraction powder patterns, the unit cell was estimated to be hexagonal with $a_o = 6.97$ and $c_o = 12.24$ Å. The compound was found to decompose into Si (ss.) and SiB_6 at temperatures in excess of 1269 ± 10°C. No evidence was found which would indicate the above process to be an incongruent melting process.

Evidence was found which confirmed the report of the solubility of boron in silicon. The extent of the solid solubility was not determined.

The compounds appeared to be black in color. They were found to have a hardness between that of agate and B_4C. They were found to be insoluble in oxidizing acids; however, they could be dissolved in a mixture of HF and HNO_3 acids. No difficulty was found in fusing the compounds with Na_2CO_3.

B. Pressure-Composition Diagrams

The pressure-composition diagrams have already been presented in Figures 12, 13, and 14; therefore, only the important features will be presented in this section. All of the phases were found to vaporize silicon preferentially. Since the vapor consisted almost exclusively of silicon and the nature of silicon vapor had been previously reported in the literature, it was concluded that the vapor consisted primarily of monatomic silicon atoms.

C. Summary of the Vapor Pressure and the Thermodynamic Values for the Vaporization and Formation of SiB_6

A least squares fit of the logarithm of the vapor pressure of SiB_6 as a function of the reciprocal of the absolute temperature gave the following equation:

$$\log P = \frac{-26009 \pm 573}{T} + 8.142 \pm 0.289 \qquad (39)$$

The second law method gave a value of 119.02 ± 2.6 kcal/mole for the enthalpy and a value of 36.53 ± 1.29 e.u. for the entropy of the vaporization of SiB_6 into Si (g) and B (c). The third law method gave a value of 113.4 kcal/mole for the enthalpy of vaporization and a value of 33.85 e.u. was estimated for the entropy of vaporization at 1900°K. The third law values were judged to be more reliable and they were used to obtain the values of 112 kcal/mole and 32.36 e.u. for the enthalpy and entropy of the process 298°K. For the enthalpy and entropy of formation of SiB_6, a value of -7.00 kcal/mole and 1.33 e.u. were calculated. From the enthalpy and entropy of formation, it is apparent that SiB_6 is not a compound with high stability.

VII SUGGESTIONS FOR FURTHER RESEARCH

A research project is never completed. The findings of one research project enable the solution of another problem to be attempted. In the course of research many interesting related problems are noted. Some of the problems which might be considered for further research will be noted here.

A search might be made to find additional compounds in the silicon boron system which are stable at temperatures which were not investigated in the course of this research.

Perhaps a more interesting field of research would be an attempt to obtain single crystals of SiB_3 and SiB_6 which could be used in a study of their crystal structures. Cline (11) reported the growth of SiB_6 single crystals from the melt; however, he has not yet reported the position of the atoms in the unit cell.

It should be possible to grow single crystals of both substances from the interaction of silicon vapor with boron crystals. In all of the preparations carried out in the course of this research amorphous boron was used. If one were to use instead of amorphous boron a few large lumps of crystalline boron, one should be able to decrease the proportion of sites of nucleation of attack of the silicon and obtain single crystals of a sufficient size.

In the course of this research, the vapor pressure of SiB_3 was only qualitatively measured. It might be possible to measure the vapor pressure of SiB_3 by effusion method and to determine the amount of material which had effused by the weight loss of the crucible. A better method would be to use collection targets and determine the amount of deposit on the target by the use of a radio active isotope (Si^{32}, $t_{1/2} = 300y$). The method of silicon analysis used in this research would be unsatisfactory, since it is insufficiently sensitive to use in the measurement of the vapor pressure of SiB_3.

In order to determine the heat of formation of SiB_6 interaction studies might be carried out with graphite, zirconium, titanium, and calcium. This would establish the heat of formation of SiB_6 with respect to the heats of formation of the borides of the above compounds.

It might be desirable to determine the heat of formation of SiB_6 by solution calorimetry. Oxidizing acids would not be satisfactory for such an experiment because of the tendency of SiB_6 to form a protective coating of SiO_2. The use of BrF_3 might be a possible substance which could be used to dissolve SiB_6.

Finally, since the silicon boron system, the boron carbon system, and the silicon carbon system have been studied; it should be interesting to study the ternary system, silicon, boron and carbon.

APPENDIX A

EQUIPMENT LIST

(E 1) Molybdenum crucible, 1 1/4" o.d. x 2" high x 0.040" thick, Fansteel Metallurgical Co.

(E 2) Tantalum spinnerets, 1/2" o.d. x 1/2" high x 0.020" thick, Fansteel Metallurgical Co.

(E 3) Spectroscopic Graphite Electrodes, Regular Grade, 1" x 12", National Carbon Co.

(E 4) Quartz tubing, 10 mm. standard wall, Lamp Dept., General Electric.

(E 5) Alumina crucible, recrystallized, 3/4" o.d. x 1" high, 3/32" thick, Morganite Inc.

(E 6) Magnesia crucible, 3/4" o.d. x 1" high x 1/16" thick, Corning Glass Works.

(E 7) Zirconia crucibles, stabilized, 3/4" o.d. x 1" high x 3/32" thick, Titanium Alloy Manufacturing Co.

(E 8) Silicon carbide crucible, graphite bonded, 3 5/8" x 3 1/4", Ross-Racony Crucible Co., crucible was constructed by drilling 1/4" hole in a 1/2" disc of the above crucible.

(E 9) Boron nitride rod, 3/4" dia. x 12", Carborundum Co.

(E10) Carver laboratory press, ser. no. 14902-48, Fred S. Carver, Inc.

(E11) Titanium diboride, 100 mesh, B 28.2%, Ti 65.1%, C 1.0%, Norton Company.

(E12) Zirconium diboride, 100 mesh, B 17.9%, Zr 76.0%, C 0.8%, Norton Company.

(E13) Tantalum, reagent grade, 99.8%, 400 mesh, Fansteel Metallurgical Corp.

(E14) Boron, amorphous, grade AA, 325 mesh, lot 1758, C 0.07%, Fe 0.16%, B 99.56% (B-9); lot 1414, C 0.10%, Fe 0.16%, B 99.60% (B12A), Cooper Metallurgical Associates.

(E15) X-ray diffraction equipment: X-ray diffraction unit, type no. 12045; powder cameras, 114.59 mm. dia., type 52056, ser. no. 57-607 (no. 1), 57-601 (no. 3), and 58-662 (no. 5); film illuminator and measuring device, type no. 52022, ser. no. 57-324; wide range precision goniometer, type 42202, ser. no. 57-883; X-ray tube type 32112, ser. no. 25100 (Cu-2); X-ray tube, type 32112, ser. no. 24604 (Cu-1); Phillips Electronics, Inc., Instrument Div.

(E16) Quartz disc, 1 1/8" diameter x 3/8" thick, Lamp Dept., General Electric Co.

(E17) Mechanical vacuum pump, Kinney Compound High Vacuum, size CVD 556, Kinney Mfg. Co.

(E18) Diffusion pump, oil, MCF-300; oil, octoil-S, Consolidated Electrodynamics.

(E19) Stopcock grease, Lubriseal, high vacuum formula, Arthur H. Thomas Co.

(E20) "O" rings, neoprene, Linear Inc.

(E21) Copper to glass seal, 1 1/4" dia., Ace Glass Co.

(E22) Wax, hard, type W, Apiezon, Metropolitan-Vickers Electrical Co., Ltd.

(E23) Pirani Gauge, PG-12, serial no. 3034, Consolidated Electrodynamics.

(E24) Cold cathode vacuum gauge, model no. 100-A, Miller Laboratories.

(E25) Logarithmic ionization gauge, built from wiring diagram from Radiation Laboratory, University of California - Berkeley, H. P. Robinson.

(E26) Electronic Induction Heater, Type HM-20-L1, 20 KW, General Electric.

(E27) Voltage regulator, dry-type, induction, GE1-43278, General Electric.

(E28) Optical Pyrometer, model 8626-6, ser. no. 1524976, Leeds and Northrup Co., (no. 4).

(E29) Prism, silvered tank prism, 146 x 53 x 38 mm., no. 3004, Edmund Scientific Co.

(E30) Window, constructed from Pyrex optical flat plate, 8" x 8" x 1/8", H. S. Martin Co.

(E31) Silicon, solar grade, E. I. DuPont De Nemours Co., (Si-2).

(E32) Steel sleeve mortar, 15 mm., Plattner Diamond, E. H. Sargent and Co.

(E33) U. S. Standard Screen Sieves, Newark Wire Cloth Co.

(E34) Mortar and Pestle, B_4C, Robert Marks Co.

(E35) Comparator, Model M 1201-30B, ser. no. 310, Gaertner Scientific Corp.

(E36) Micrometer, Miller Falls Co.

(E37) Caliper, vernier, cat. no. 123, L. S. Starrett Co.

(E38) Cathetometer, ser. no. 362A, Gaertner Scientific Co.

(E39) Clock, Time-it, direct reading in units of 0.01 min., Precision Scientific Co.

(E40) pH meter, cat. no. 7664, ser. no. 1313141, Leeds and Northrup Co.

(E41) Colorimeter, Electrophotometer, ser. no. 5383, Fisher Scientific Co.

(E42) Interference filter, 820 mμ , 9 half width, Bausch and Lomb.

(E43) Sodium carbonate, Calcined-Dry-Purified, cat. no. S-261, Fisher Scientific Co.

(E44) Resistor, precision, 10 ohm, ser. no. 243570, Leeds and Northrup Co.

(E45) Potentiometer, model no. 8662, ser. no. 779503, Leeds and Northrup Co.

(E46) pH meter, model G, ser. no. 9248, Beckman Instruments, Inc.

(E47) Clock, calibrated in 0.1 sec., model S-10, The Standard Electric Time Co.

(E48) Boric Acid, reagent grade, minimum assay 99.5% H_3BO_3, lot no. 52440, Merck and Co., Inc.

APPENDIX B

CRYSTAL DATA

Phase	Molecules per Unit Cell	Symmetry	Parameters	Ref.
boron	12	rhombohedral	$a_0=5.06$ $\alpha=58°4'$	(37)
boron	50	tetragonal	$a_0=8.473$ $c_0=5.030$	(38)
boron	108	rhombohedral	$a_0=10.12$ $\alpha=65°28'$	(39)
silicon		cubic	$a_0=5.430$	(17)
SiB_3		tetragonal	$a_0=2.829$ $c_0=4.765$	(6)
SiB_3		hexagonal	$a_0=5.52$ $c_0=12.70$	(8)
SiB_3		hexagonal	$a_0=3.10$ $c_0=12.55$	(8)
SiB_3		hexagonal	$a_0=6.97$ $c_0=12.24$	this work
SiB_6		cubic	$a_0=4.150$	(10)
SiB_6		orthorhombic	$a_0=14.392$ $b_0=18.267$ $c_0=9.885$	(11)
SiB_{12}		orthorhombic	$a_0=11.10$ $b_0=14.79$ $c_0=10.12$	(14)

APPENDIX C

BEST FILMS

Phase	Film No.	Phases Present
Al_2O_3	C- 262	Al_2O_3
boron	C-1392	boron, (108 atom)
BN	D- 302	BN
B_4C	C- 334	B_4C
graphite	C- 364	C
CaB_6	C-1026	CaB_6, Si
KCl	C- 459	KCl
MgO	C-1143	MgO
silicon	C- 365	Si
SiB_3	C-1531	SiB_3, Si
SiB_6	C-1444	SiB_6, B (ss.)
SiC	C- 47	SiC, B
TaB_2	C-1170	TaB_2
TaN	C- 733	TaN
TiB_2	C-1203	TiB_2, SiB_6
ZrB_2	C-1109	ZrB_2
ZrO_2	D- 72	ZrO_2

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