EQUILIBRIUM PRESSURES AND STABILITIES IN THE MOLYBDENUM - BORON SYSTEM

by

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TABLE OF CONTENTS

A. Introduction

The objective of this investigation was to study vaporization processes in the molybdenum - boron system for the purpose of determining equilibrium pressures and stabilities of the borides and possible gaseous compounds.

Quantitative data concerning thermodynamic stability and equilibrium pressures are of practical value in choosing materials of construction for use at high temperatures and at low pressures, and are of theoretical value in that they represent a contribution to knowledge of a group of compounds for which relatively little quantitative data are available.

The molybdenum - boron system was chosen because it is representative of a group of refractory two-component systems, one component of which is a transition metal, and the other of which is one of the light non-metals (1,2,3,4,5,6,7). These systems are characterized by their hardness, high melting points, metallic luster, high electrical conductivity and very frequently by nominal compositions of solid phases having little apparent relationship to the normal valence numbers of the elements.

Molybdenum and boron form a number of solid phases which have the general properties described above. Three phases are stable at room temperature, Mo_2B, MoB, and Mo_2B_5 (7,16a,16b), the last two having high temperature forms and extensive homogeneity ranges. A sixth phase, Mo_3B_2, isomorphous with Cr_3B_2, is stable

only at high temperatures and disproportionates at low temperatures into Mo_2B and MoB (9). Boron is not soluble to a detectable extent in molybdenum. The melting temperatures range from about 2100 to 2350°C. (11).

Of the various methods of determining stabilities or free energies of formation, that based on vapor pressure data is the most applicable to refractory compounds of the type being considered (19). The factors which favor the use of such data are that a wide variety of methods for measuring pressures over a wide range of pressures and temperatures exist (20) and the stabilities are logarithmic functions of pressures. On the other hand, determination of stabilities from thermal data is complicated by the difficulty of obtaining accurate high temperature heat capacities, the inertness of the compounds, and the difficulty of obtaining reaction products of definite composition (23).

The methods of measuring vapor pressures which were considered were: (a) Langmuir's rate-of-evaporation method, (24) (b) Knudsen's effusion method (25) (c) manometric or static method, (26) (d) the transpiration method, (22) and (e) methods based on mechanical force measurements. The last three methods were eliminated for various reasons as follows: the manometric techniques employ apparatus having very close mechanical tolerances which would be very difficult or impossible to attain at very high temperatures; the theoretical

study of the transpiration method carried out by Lepore and Van Wazer indicated that diffusion effects would render the method not suitable for use at the high temperatures and low pressures to be expected; and the low forces to be measured by the reaction method would introduce mechanical difficulties. Observations made during preliminary studies indicated that the Langmuir method would prove to be most advantageous in the region of composition studied.

It may be pertinent to point out here that the experimental work to be described in the following sections of this report was not carried out in the chronological order in which the topics are arranged in the table of contents. Thus, various parts of the work described under each of the major sections were carried out over the entire period of this investigation. For example, analytical methods were tried and used as the need for them became evident during the course of the work. Heating arrangements were devised and tried as more information concerning the system was accumulated and requirements became clear.

The experiments on which calculations of the stabilities of Mo_2B, MoB, Mo_3B_2 and MoB_2 were based are described very briefly below in the chronological order in which they were conducted.

(1) A group of five samples of composition ranging from $MoB_{1.0}$ to $MoB_{2.2}$ were heated simultaneously in a molybdenum crucible.

The samples were suspended inside individual cylindrical shields which served to isolate the samples from each other. These experiments were carried out in June, 1951, and are recorded in Notebook I, pp 38-48 and pp 57-58.

(2) Cylindrical samples approximately 19 mm diameter and 16.5 mm in height having a MoB core and a Mo_2B surface were heated in a Langmuir experiment to obtain rate-of-evaporation data. These experiments were carried out during the period February to May, 1953, and the data are recorded in Notebook V, pp 15-76.

(3) A cylindrical sample of Mo_2B was heated in a manner similar to that described in (2). Information obtained in this and the preceding group of experiments showed that Mo_2B is not a constant evaporating composition and also permitted making calculations of stability of Mo_2B. These experiments were carried out in May, 1953, and the data are recorded in Notebook V, pp 82-87 and Notebook VI, pp 2-5.

(4) Experiments on a MoB cylinder were carried out in which the temperature and duration of heating were limited to those at which Mo_2B and MoB could exist at the surface. The reaction

$$2MoB_{0.96}(s) \rightleftarrows Mo\ B(s) + 0.92B(g)$$

could be studied in this way. These experiments were carried out in May, 1953, and the data are recorded in Notebook VI, pp 94-99 and Notebook VI, p 1.

B. Apparatus and Materials of Construction

A description of the equipment and materials used for this work appears elsewhere (28), however, a brief resume of the main features of the vacuum induction furnace used for the major fraction of the work is given below.

The line, designated "apparatus no. 2", was characterized by use of a high-speed pumping system and placement of the sample directly above the diffusion pump to obtain the most direct possible gas flow, to reduce "dead volume" to a minimum, and to obtain simplicity of design. A two-piece baffle between the oil diffusion pump and the cell minimized back diffusion and kept powders and other substances from falling into the pump. Pressures were read by means of a Pirani and an ionization type gauge, and a utility port was provided for attaching a McLeod gauge for calibration or for introduction of electrical leads, leaks or inert atmospheres.

High frequency power for heating was derived from a 6 KW Ajax electrothermic arc type converter operating at about 25 KC. A group of four work coils of various sizes made possible a choice of heating conditions.

Provisions for automatic temperature control and temperature recording, and the circuit used to calibrate optical windows are also described in another place (28). The automatic temperature control equipment was not used because its use resulted in excessive decrease in attainable temperatures.

Crucibles and radiation shields were made of tantalum and molybdenum rod and sheet and of spectroscopic grade graphite rod. Tantalum and molybdenum rod of various diameters up to 1/8 inch was available and was used as supports for assemblies of various kinds. A complete listing of available materials of construction is also given in the report cited above.

Two Leeds and Northrup disappearing filament optical pyrometers which were certified by the National Bureau of Standards were given the laboratory designation "no. 1" and "no. 2" and were used with apparatuses no. 1 and no. 2 respectively. Temperature readings were estimated to be accurate to $\pm$ 20° C.

C. Analytical Methods

The analytical procedures considered essential to this investigation were: (a) those for the assay of molybdenum and boron in the raw materials and boride preparations, (b) methods for the determination of vapor compositions, and (c) a method for identifying solid phases. In addition a number of auxiliary methods were found helpful for such purposes as identifying and estimating impurities and estimating effectiveness of purification processes and will therefore be described briefly.

1. Assay of Molybdenum and Boron

Samples sufficient to give about 0.25 gm of molybdenum and about 30 to 40 mgms of boron per aliquot were dissolved in a mixture of HCl and HNO_3 or HCl and H_2O_2 in a pyrex flask fitted with a reflux condenser to avoid mechanical loss. The mixed acids were about 1 N in HCl and 2 to 6 N in HNO_3. The quantity of acid was kept to a minimum required to effect solution so that a high HNO_3 concentration would not interfere with subsequent boron determinations by oxidizing the indicators. If H_2O_2 were used, the reagent was added in 2 to 5 ml portions as required. The latter reagent was slower than the former but could be decomposed by heating for 5 to 10 minutes after making the solution alkaline. Boride and boron solutions were made alkaline to remove iron, which could be estimated colorimetrically. The intensity of the colored complex formed by ferric iron and KCNS in HCl could be compared visually

with standards prepared in a similar manner. No effort was made to remove iron or to estimate that metal during assays of molybdenum powder because the specifications for the raw material showed negligible quantities of iron. After removal of iron from the boride or boron solutions, the solutions were made acid and transferred to volumetric flasks, made up to the appropriate volume, and aliquots taken as required.

The molybdenum was assayed by the lead molybdate method described by Scott (29). It should be noted that molybdenum forms poly-acids and a silico-molybdate complex the destruction of which may require prolonged digestion of the lead molybdate precipitate. At least two hours digestion at or near boiling temperature is recommended. Molybdenum analyses were found to be reliable to about 0.2% relative to total molybdenum, although failure to wash precipitates thoroughly or to digest them sufficiently could cause errors as great as 2%.

Boron was determined by the method Blumenthal described for use with transition metal borides (8). The use of mixed acids instead of a carbonate fusion to effect solution, and adjustment of pH with barium hydroxide to precipitate molybdenum (30) were the modifications in the method as originally given. An aliquot of the acidified, iron-free solution as prepared above was diluted to about 100 to 125 ml and sufficient barium carbonate added to

neutralise the major fraction of HCl. Barium hydroxide was then added to adjust the pH to 8 or 8.5 using Hydrion paper as indicator, thus precipitating molybdenum as berium molybdate which could then be removed by filtering. The filtrate from the molybdate precipitation was acidified slightly with HCl and boiled for about one minute to remove CO_2, and the excess acid was then neutralized with NaOH using a mixed indicator. Eight grams of mannitol was then added and the boric acid titrated as the mannitol complex.

The boron determinations on samples analyzed as above were reliable to about 1% relative to the boron content. The chief source of error appeared to arise from incomplete removal of molybdate and manifested itself by giving a poor end point when the excess HCl was neutralized. End points were usually sharp unless the solution temperature dropped, consequently it was desirable to maintain the temperature at 60 to 80° C. as recommended by Blumenthal.

2. Vapor Compositions

Analytical information concerning compositions of vapors was needed to study vaporization processes and to calculate partial pressures of boron and molybdenum in rate-of-evaporation experiments. Some information could be obtained from weight loss and composition change data obtained by the methods described above, however such determinations were not always feasible, particularly in the experiments to determine the stability of Mo_2B. The small

weight losses and small composition changes to be expected in these experiments necessitated the use of methods applicable to the small quantities of sublimates.

Spectrophotometric methods were tried but proved to be unsatisfactory. Two methods were tried for the metal, the first being based on the formation of a peroxy-acid having an absorption maximum at 330 millimicrons (31) and the second based on the formation of a complex by Mo(V) and KCNS in acid medium (32). The instability of aqueous tantalates interfered with both methods by virtue of the tendency of molybdenum to be carried down by the tantalum on which sublimates were condensed. Boron could not be determined accurately in the presence of tantalum, the difficulty being attributed to incomplete removal of the metal by the method outlined earlier. Efforts to determine boron by use of a colorimetric method utilizing quinalizarin as reagent proved unsuccessful because of inability to observe any color change. As a consequence of the difficulties above, it was necessary to resort to spectroscopic methods for the desired analyses.

Two spectroscopic methods were employed to determine the boron - molybdenum ratio in vapors obtained during experiments to determine the stability of Mo_2B. The same set of four standards could be used for preparation of calibration curves for both methods.

The "unknowns" consisted of tantalum radiation shields on which

sublimates of molybdenum and boron were collected. The standards were prepared to simulate as nearly as possible the expected compositions of the unknowns. It was possible, on the basis of weight-loss data obtained during experiments and approximate vapor compositions obtained from weight loss - composition change data, to estimate the probable range of concentration of boron and molybdenum in tantalum. The estimated range for boron, in weight per cent relative to tantalum, was from 0.30% to 1.10%. The boron was added to approximately 0.2 gm of tantalum sheet in the form of commercially available $TaB_{1.74}$, the assay of which had been confirmed within experimental limits of error. The boron content was calculated on the basis of total tantalum. The value of the molybdenum content was kept constant at a figure of 2.0 weight per cent relative to tantalum and was within the estimated range of molybdenum concentration expected in the unknowns.

The unknowns and standards were fused in approximately ten times their weights of a fusion mixture consisting of 9 parts by weight of K_2CO_3 and one part KNO_3. After the melts were crushed, they were subjected to the usual operations of emission spectroscopy. Intensities of lines were read by means of a densitometer. Exposure of the film, arcing conditions, and other operations were kept as nearly constant as possible. The unknowns were determined in two groups and a set of standards was run with each group.

The first method of determination of vapor composition made use of the tantalum itself as an internal standard and was similar to that described by Brode (33). In this method, the boron content of the shield was determined and the molybdenum obtained by difference. In the second, the boron - molybdenum ratio was determined directly. The fact that the total concentrations of the standards and unknowns were comparable with respect to both molybdenum and boron made the method feasible and gave approximate agreement with the first method. Because both methods suffered from wide variations in optical density of emission lines, neither method could be selected as being superior so results of the two analyses run on each unknown were averaged to obtain the values used for computation of compositions.

3. Identification of Solid Phases

The identification of solid phases for such purposes as obtaining assurance of complete reaction during a boride preparation, and determining compositions of surfaces, could be reliably and quickly made with a General Electric XRD - 3 x-ray diffraction apparatus equipped with a spectrogoniometer. This apparatus traces out a plot of x-ray intensities vs 2θ on a strip chart on which angle marks are made.

The copper tube and a nickel filter were used to examine the borides of molybdenum. The procedure for powders was as follows: The powder, of about 200 mesh, was sprinkled in a thin layer about

1/4 inch wide and 1 1/4 inch long down the middle of a vaseline-coated glass microscope slide. The slide was then placed in position on the spectrogoniometer and the x-ray detector allowed to scan through an increment of 2 θ from about 20 to 80 degrees. Surfaces of cylinders were examined in a similar manner though alignment of the surface in the beam was made visually. A run could be made in this manner in about 40 to 45 minutes.

Deviations from values of 2 θ calculated from literature data were about 0.1 or 0.2 degree for powders, and about 0.4 degree for cylinders. These deviations were attributed to poor alignment of the sample and apparatus, variations in thickness of samples, and to personal error in reading angles. These deviations caused no difficulty in making identifications. Values of 2 θ for Cu K_α radiation and relative intensities of reflections for molybdenum, Mo_2B, MoB, and Mo_2B_5 are given in Table 1. The values of 2 θ were calculated from Kiessling's data (7) for Cr($K\alpha_1$) radiation and then recalculated for Cu($K\alpha_1$) radiation according to the equation

$$(\sin \theta)_{Cu} / (\sin \theta)_{Cr} = \lambda Cu / \lambda Cr$$

where $\lambda_{Cu} = 2.290$ Å and $\lambda_{Cr} = 1.541$ Å. No patterns for boron could be obtained.

4. Auxiliary Methods

In addition to the methods discussed above, visual estimates of impurities evolved from samples were made from photographic plates

obtained by emission spectroscopy. Quantities of iron of the order of 5 to 10 mgms evolved during purification runs could be estimated by dissolving sublimates in HCl, oxidizing the iron to the trivalent form, precipitating with NaOH and comparing the precipitates with those prepared by use of known volumes of standard iron solutions. Molybdenum in sublimates could be identified and estimated by use of the $SnCl_2$ - KCNS method.

Table I

X-Ray Diffraction Data for Molybdenum and Molybdenum Borides

Mo Cubic B.C.		Mo_2B Tetragonal		MoB Tetragonal		Mo_2B_5 Rhombohedral	
40.8	vs	22.3	w	21.2	w	24.6	s
58.8		32.2	m	29.2	w	34.7	w
73.9	s	38.0	s	32.9	s	36.3	
87.8	w	41.2	s	39.3	s	38.9	w
101.7	w	44.6	w	42.5	vs	40.0	m
		50.6	m	42.6		43.6	w
		52.2	w	47.4	m	48.1	m
		61.4	vw	52.7	w	52.7	w
		63.6	vw	57.1	w	53.1	
		66.3	m	59.5	m	58.1	
		67.6	vw	60.0	vw	62.2	s
		70.7	s	63.8	w	63.8	
		72.3	w	66.0	w	64.7	
		73.2	m	67.6	w	67.4	vw
				67.8	w	68.4	s
				68.8	vw	71.2	w-m
				69.7	w	73.2	w
				70.0	m	73.6	w
				72.7	w-m	75.9	w
				75.8	w-m	82.3	s
				78.4	w		
				78.6	w		

D. Preparation of Borides

The borides were prepared directly from commercially available elements of high purity (14). The availability of the raw materials in powdered form and the availability of a vacuum induction furnace made this method feasible and convenient (13).

1. The Raw Materials

The molybdenum powder, of 400 mesh, was obtained from the Fansteel Metallurgical Co. and was specified as being of 99.9% purity when freshly prepared. The manufacturer's specification sheets for this material indicated that oxygen was the principal impurity and that minor impurities were nitrogen, carbon, iron and nickel in trace amounts. The powder is subject to oxidation on exposure to air over prolonged periods of time. The assay 1 1/2 years after purchase was 99.4% after the sample was outgassed at 1000° C. for 5 minutes in a vacuum induction furnace. A weight loss of 0.3% occurred during the outgassing. Reference to the list of batches of molybdenum and boron used in this work shows that the assay of molybdenum was higher at earlier periods of time. It is probable that assays for molybdenum were slightly low because of adsorption of atmospheric vapors, however it is apparent that molybdenum powder should be used quickly, or should be stored in a vacuum in order to realize its initial high purity.

The 325 mesh boron powder was obtained from the Cooper Metallurgical Co. and from the Fairmount Chemical Co. Both manufacturers

Table II

Summary of Information Concerning the Molybdenum and Boron

Molybdenum

Batch No.	Mfr. and specifications	Remarks
1	Fansteel. 99.9%, O_2 and N_2 main impurities	Hydrogen reduced. 1 lb. recv'd 3/51. Assay 99.5% after 7 mo. Assay 99.4% after 1 1/2 yrs.
2	Fansteel.	2 lbs. recv'd 3/53.

Boron*

1	C. B = 99.13% Fe = 0.60% C = 0.22%	10 gms recv'd 11/50. Assay 98-99% after drying in lab. vacuum oven.
2	C. B = 99.12% Fe = 0.60% C = 0.12%	10 gms recv'd 5/51
3	C. B = 99.20% Fe = 0.35% C = 0.25%	15 gms recv'd 3/52. Spectroscopic estimates showed Mg and Si as additional impurities; % Mg x %Si.
4	F.	10 gms recv'd from A.W. Searcy, Purdue Univ. "No great weight loss on heating at 1900° C." Recv'd 6/52.
5	F. B = 99.10% Fe = 0.40% C = 0.30%	50 gms recv'd 11/24/52. This batch was dropped. Assayed 12/20/52. 95.5% B. 1% Fe.
6	F. B = 99.10% Fe = 0.40% C = 0.30%	50 gms recv'd 3/53.

* C. = Cooper Met. Co.; F. = Fairmount Chem. Co.

claimed purities of 99.0% or higher, and stated that iron and carbon were the principal impurities. Chemical and spectroscopic analyses verified their claims within the limits of the analytical procedures used, though carbon was not determined. The assays were made on samples which had been outgassed in a vacuum induction furnace by heating them to about 1700° C. for about ten minutes with a loss of weight of 3 to 4%. Batch No. 5, of fifty grams, which had been obtained from the Fairmount Chemical Co., was dropped on a wooden floor in poor condition, where the glass container broke. The batch was recovered with care being taken to minimize the amount of dirt and glass picked up, and the material was then screened through a 300 mesh screen to remove glass. Its assay was 93.5% after outgassing. About 1% of iron and comparable quantities of silicon, calcium and magnesium were found as impurities in this batch.

2. General Procedure

The first step in a preparation consisted in outgassing the raw materials. The molybdenum and boron were each compacted with only sufficient pressure to prevent their being blown out of the crucible when the mechanical forepump was turned on. Molybdenum was heated for 10 minutes at about 1000° C. in a molybdenum crucible with a weight loss of about 0.3%. Boron was heated in a similar manner to about 1600 to 1700° C. with weight losses of 3 to 4%.

Heatings were carried out with the diffusion pump in operation. Use of high compacting pressures and higher temperatures than those indicated resulted in excessive sintering with attendant difficulty in crushing and grinding.

After the outgassing, the materials were crushed, weighed out and mixed. An excess of boron was taken to compensate for impurities, about 3% usually being sufficient when 99% boron was used. The powders were mixed first in a glass bottle of appropriate size and then passed three times through a 50 mesh screen to ensure thorough mixing.

The mixed powders were compacted under about 6,000 lbs of pressure per square inch and heated in vacuum in molybdenum crucibles. The mixtures were heated slowly to eliminate most of the occluded gases and vapors, and the temperature was then raised to about 1000 to 1200° C. to effect reaction. The occurrence of reaction was marked by sudden rises in temperature and the expulsion of additional vapors. In the preparation of 25 to 35 gm batches of Mo_2B, temperature rises of 50 to 100° C. were noted, and in the preparation of comparable quantities of MoB, temperature rises of about 300° C. were found. Large batches of MoB_2 were not made, but observations suggest that the reaction is also clearly exothermic. If the violence of the reaction did not blow the lid off the crucible, the mass was heated to 1400 to 1800° C. to effect some purification. With the exception of carbon, the impurities are more volatile than the

borides.

After the borides were formed, they were subjected to examination by x-ray diffraction to make sure that reaction was complete, and to chemical assay. If these examinations showed the need for adjustment of composition, the appropriate quantity of molybdenum, boron, or other boride of known composition was added and mixed and the mixture was homogenized by heating for about 10 minutes. Mo_2B preparations were heated to about 1400 - 1500° C. and MoB samples were heated to 1800 - 1900° C. Excessive sintering took place if the batches were heated to higher temperatures, so these values were not generally exceeded unless the experiment for which the material was intended did not require crushing and grinding.

It may be pointed out that x-ray examinations of the reaction products showed that reaction between molybdenum and boron, or between the elements and borides, was complete under the conditions employed, and that a given mixture of the elements produced, within the limits of uncertainties regarding purities, reaction products consistent with published data on phase compositions.

3. Purity

The effects of impurities in the samples are: (a) to change physical and thermodynamic properties such as electrical conductivity and thermodynamic activities, (b) to cause weight loss errors as a result of volatilization of oxides or other contaminents, and (c) to cause composition changes in vaporization experiments. Thus,

excessive loss of boron could take place by virtue of the formation of stable boron oxides and their subsequent volatilization. The amount and nature of the impurities and the effectiveness of procedures for their removal were therefore of considerable interest and will be discussed below.

Carbon and the metallic impurities were introduced primarily through the boron. Oxygen and oxides were derived primarily from exposure of the materials to the air. With the exception of carbon and carbides, which do not have any solubility in the borides (16b) and would therefore not cause errors of the type outlined above, all the important impurities are more volatile than the borides. It was therefore possible to take advantage of the high temperature heatings in the vacuum induction furnace used in the preparation of borides and the fabrication of cylinders to effect purification.

It was necessary to evaluate the effectiveness of these operations indirectly. The limitations on the accuracies of the methods for assaying molybdenum and boron, and the introduction of impurities from the mortars when the hard samples were crushed and ground made sufficiently accurate estimates, particularly of oxygen, impossible. The desired estimates were based on assays of the dried starting material, assays of the borides at early stages of fabrication, weight losses found during various sintering operations, weight gains of cylinders when exposed to the air, spectroscopic and chemical estimates of impurities in sublimates found on the walls of the cells after heatings.

On the basis of the information such as listed above, the general pattern of the purification procedure has been deduced. Freshly prepared borides had a minimum calculated purity of 99.0%, based on assays of dried molybdenum and boron but were still sufficiently contaminated as to make them unfit for use in most vaporization studies. They were also subject to adsorption of atmospheric vapors and gases and subsequent oxidation. Sintering operations were carried out in the vacuum furnace with the diffusion pump in operation. It is estimated that as much as 0.2 - 0.3% weight losses, in the form of adsorbed vapor, were effected by the pumping down and initial warm up. The estimate is based on estimated "average" pressures, pumping speeds and times for outgassing. Sintering at high temperatures caused additional outgassing, and the elimination of the metallic impurities and oxides, and also tended to reduce susceptibility to atmospheric contamination. This type of contamination, which was considered to be the most troublesome, manifested itself as weight gains on exposure to air and had the effect of giving high rates-of-loss and producing composition changes by virtue of combination of the boron of the sample with oxygen. Whether oxidation occurred at room temperature or took place when samples were heated is not known, though probably both effects took place and were followed by loss of boron in preference to the loss of molybdenum. The effect of the atmosphere was reduced by vigorous sintering, no doubt as a result of the reduction in internal area accompanying the

increase in bulk density.

An estimate of purity of samples as used for experiments can be made by using as an example a typical cylinder prepared for Langmuir rate-of-evaporation experiments. The samples had been made from a batch of $MoB_{0.93}$ prepared from molybdenum assaying at 99.4% and boron assaying at 95.5%. The calculated purity on a dry basis was 99.0%, assuming no purification took place during preparation of the boride powder. The iron content was about 0.1% as determined by chemical methods, and spectroscopic estimates based on the iron as an internal standard showed that calcium, magnesium and aluminum were present to the extent of 0.2 - 0.3%, together with trace amounts of other substances. Carbon was not determined though it amounted to about 0.05%. The cylinders were pressed using twenty-five gram portions and the green compacts heated for about 10 - 15 minutes at 1800 - 1900° C., with weight losses of about 75 mgm, or 0.3%. The chemical assay for boron and molybdenum showed a purity of 99.5%. After the "presintered" cylinders were drilled, they were subjected to a series of heatings at more elevated temperatures, of the order of 2100° C. to decontaminate and shrink them. Weight losses of the order of 150 - 200 mgms occurred under conditions such that only 50 - 60 mgms loss of boride could have occurred. From the chemical analyses performed on the sublimates obtained for a group of experiments carried out at about 1400 - 1600° C., at which virtually no boride would volatilize, it was concluded

that deoxidation occurs by a combination of simple evaporation of oxygen and vaporization of boron oxides, with very little molybdenum oxide loss. It is thus possible to conclude that the treatment accorded the samples in question rendered them of a purity of 99.9 - 99.8%. Other samples, prepared from fresher batches of molybdenum and less contaminated boron could be expected to have impurities to the extent of less than 0.1%.

E. Fabrication and Heating of Boride Cylinders

1. Choice of Methods

Three methods for preparing boride cylinders or rings were considered: (a) by powder techniques, (b) by casting, (c) by diffusion of boron into metal rings. Method (b) was discarded because of the difficulty of heating sufficiently large quantities of borides to melting temperatures and because of the absence of satisfactory mold materials. Method (c) was tried but proved unsatisfactory because of cracking caused by "swelling" as boron reacted with and diffused into the metal.

The use of induction heating was selected in preference to electrical heating of wires because of the following advantages pointed out by Johnston and Marshall (34):

(a) "hot spots" due to non-uniform diameter are avoided

(b) "end effect" or temperature gradients at the ends of wires are avoided

(c) elimination of significant changes in evaporating surface area as vaporization occurs.

(d) ease of obtaining temperature readings by sighting into "blackbody" holes eliminates the need for emissivity data.

An additional advantage is the simplicity of design of the apparatus as compared with that when electrical leads must be brought into a high vacuum system.

2. Fabrication Procedure

The object of the procedure to be described below was to prepare dense solid cylinders or annular rings of borides having one or more blackbody holes near the cylinder walls. Solid cylinders were to have small centering holes in the center of each end. Such samples were made by a combination of powder pressing, sintering and machining steps.

The design of the powder dies used in these experiments was based on specifications suggested by Brewer et al (35). A brief description of the three dies used appears in the Table below, though a more detailed description is given elsewhere (28).

Table III

Description of Powder Dies

No.	Nominal O. D. of Compacts	Remarks
1	1/2 inch	Successfully made solid cylinders and annular rings having a 1/4 inch I.D.
2	1 inch	Used to prepare solid samples. Not successful in pressing annular ring compacts.
A-107	27/32 inch	Obtained from Univ. of Cal Used to prepare solid cylinders.

The dies described above were made from "Ketos" or "Blue Chip" tool steel, except for the plunger of die No. 2. This item was made from

a high carbon steel obtained from an automobile axle and took a rough finish after hardening and grinding which may have accounted for the inability to produce the annular rings.

The boride powders, the preparation of which has been described earlier, could be compacted without the use of a binder under a pressure of 12,000 to 14,000 lbs per square inch. It was also found that no lubricant was needed if the compacting pressure was kept below the limits indicated above. In order to simplify the procedure and to avoid introduction of extraneous substances which might adversely affect the purity of the samples, neither a binder nor a lubricant was used. Compacting took place at room temperature, although a hot die was tried. Compacting was found to be good with a die that had been heated to 110° C. in a laboratory drying oven but the difficulty in handling the hot die even with asbestos gloves caused the abandonment of this procedure.

After pressing, the compacts were subjected to a "presintering" in molybdenum crucibles to cause the particles of boride to stick together well enough to allow the necessary holes to be drilled. Mo_2B samples were sintered initially at about 1500° C. and MoB samples were sintered at about 1900° C. The treatment above rendered the compacts somewhat chalky, but they could be drilled by use of high speed drills. Annular rings could also be made from the larger cylinders by turning out the center part of the cylinder on a lathe. Use of higher sintering temperatures made these machining operations impossible.

After the mechanical operations on the samples, the latter were subjected to two or more sintering heats at 2100 to 2250° C. to drive off the volatile impurities and increase the bulk density. The shrinkage accompanying the first high temperature sintering was about 30 to 35%, by volume and produced a marked hardening of the sample and resistance to abrasion and caused a decrease in susceptibility to oxydation. Samples were usually somewhat distorted as the result of uneven shrinkage, and were therefore "trued" by grinding, thus causing the need for an additional outgassing to remove impurities introduced by this operation.

The 1/2 inch diameter samples were prepared in a manner differing somewhat from the general procedure outline above in that these samples often did not need intermediate mechanical operations and therefore could be sintered at high temperatures immediately after pressing. All samples, however, were subjected to outgassing heatings immediately before they were used for data runs.

3. Results of Heating Tests

The selection of dimensions which would permit the attainment of temperatures necessary for this work was made on a trial and error basis because the lack of availability of resistivity data at the beginning and the porous nature of the samples made calculations impossible. Some of the heating tests that were carried out will be described below because they lead to suggestions that may prove helpful in future work.

The runs to be discussed were as follows:

a. Run 9. A solid cylinder 21 1/2 mm diam. x 17 1/2 mm was heated to a maximum temperature of 1630° C. The sample had not been subjected to a high temperature sintering, and was heated in line No. 2 with only a pair of tantalum end shields.

b. Run 64 C. An annular ring 2.37 cm in diameter and 1.80 cm in height, prepared by the process described above could be heated to 1300° C. with a power input to the converter of 6 KW, and to 1850° C. with a power input of 6 1/2 KW. Only graphite end shields were used.

c. Run 65 C. A ring similar to that used in b. above could be heated to 2250 to 2300° C. with a tantalum radiation shield.

The annular rings described in the preceding experiments all ultimately cracked after a number of heatings but in each case cracking did not occur until weight losses of about 2% had occurred. All experiments were carried out in line No. 2 with a quartz cell and Ajax work coil 3P1, having an I.D. of 2 3/8 inches.

It would appear that shrinkage may cause a change in resistance sufficiently great as to affect the heatability of samples. Also, the possibility exists that a smaller work coil might increase the attainable temperatures to a value at which shielding may not be necessary.

F. The Molybdenum - Boron System

1. Previous Work

Kiessling described three solid phases stable at room temperature, Mo_2B, MoB, and Mo_2B_5(7). Bertaut and Blum reported in 1951 the existence of a fourth structure, MoB_2 (10). Later, Steinitz (21) and Steinitz, Binder and Moskowitz announced the discovery (7) of a high temperature phase, Mo_3B_2, which disproportionates at low temperatures into Mo_2B and MoB, and of a high temperature form of MoB which they designated as β-MoB. The last named authors showed that MoB_2 is a high temperature form of Mo_2B_5 and has the same homogeneity range as the low temperature structure.

Steinitz and his colleagues had also measured melting points, transition temperatures and eutectic and peritectic temperatures in the system. During the course of work on vaporization properties of some of the molybdenum - boride compounds, it was possible to make observations of some transition temperatures. When the report of the other workers appeared, it was decided to repeat, in part, their study.

2. Experimental Work and Results

a. Samples

Stocks of Mo_2B and MoB were prepared according to the procedure described in the section "Preparation of Borides", and were found to have purities of 99.0% or higher. Individual samples of intermediate compositions were prepared from these two stocks and were

mixed by screening.

b. Procedure

Most of the experiments were carried out in graphite containers, as were those of Steinitz et al. Two kinds of containers, made from spectroscopic grade graphite rod, were used to heat groups of mixtures weighing 1/4 - 1/2 gram. The first consisted of a 7/8" diameter cylinder 3/4" high into which 7 holes 3/16" in diameter and 1/2" deep were drilled. The second was made by drilling a 3/16" hole 1/2" deep into a 1/4" graphite rod 5/8" long. The first was heated directly by induction and the small crucibles were packed into a tantalum heating element for induction heating.

The heatings were performed in a high vacuum system in which the maximum pressure was 2×10^{-5} mm and was usually less than 1×10^{-5} mm. The general pattern of heating in graphite was to raise the temperature rapidly to a value somewhat below the desired one and then to raise the temperature slowly. The samples were held for 2 - 5 minutes at the maximum temperature. The short time was employed to reduce possible contamination by the crucible material and to reduce composition changes that would occur on heating. The samples were examined after the heating, and if no changes were noted, were reheated to a higher temperature.

Temperatures were measured with a Leeds and Northrup Disappearing Filament Optical Pyrometer, certified by the National Bureau of Standards, by sighting through a window at the top of the vacuum

system into the central hole in experiments with the graphite cylinders, and into one of the graphite crucibles in experiments with these in the tantalum heating element. Some observations were made during vaporization studies conducted by heating samples in tantalum cruci les allowing minimum contact with the compacts and are pertinent to this investigation. In these cases, temperatures were read by sighting directly into the crucibles through an effusion orifice. The reproducibility of temperature reading was about ± 5 degrees. Numerous comparisons of pyrometer readings showing agreement among several workers in this laboratory have been made. To the observed readings the certification corrections and window corrections were applied in the usual way. The absolute uncertainty of the temperature measurements is of the order of twenty degrees.

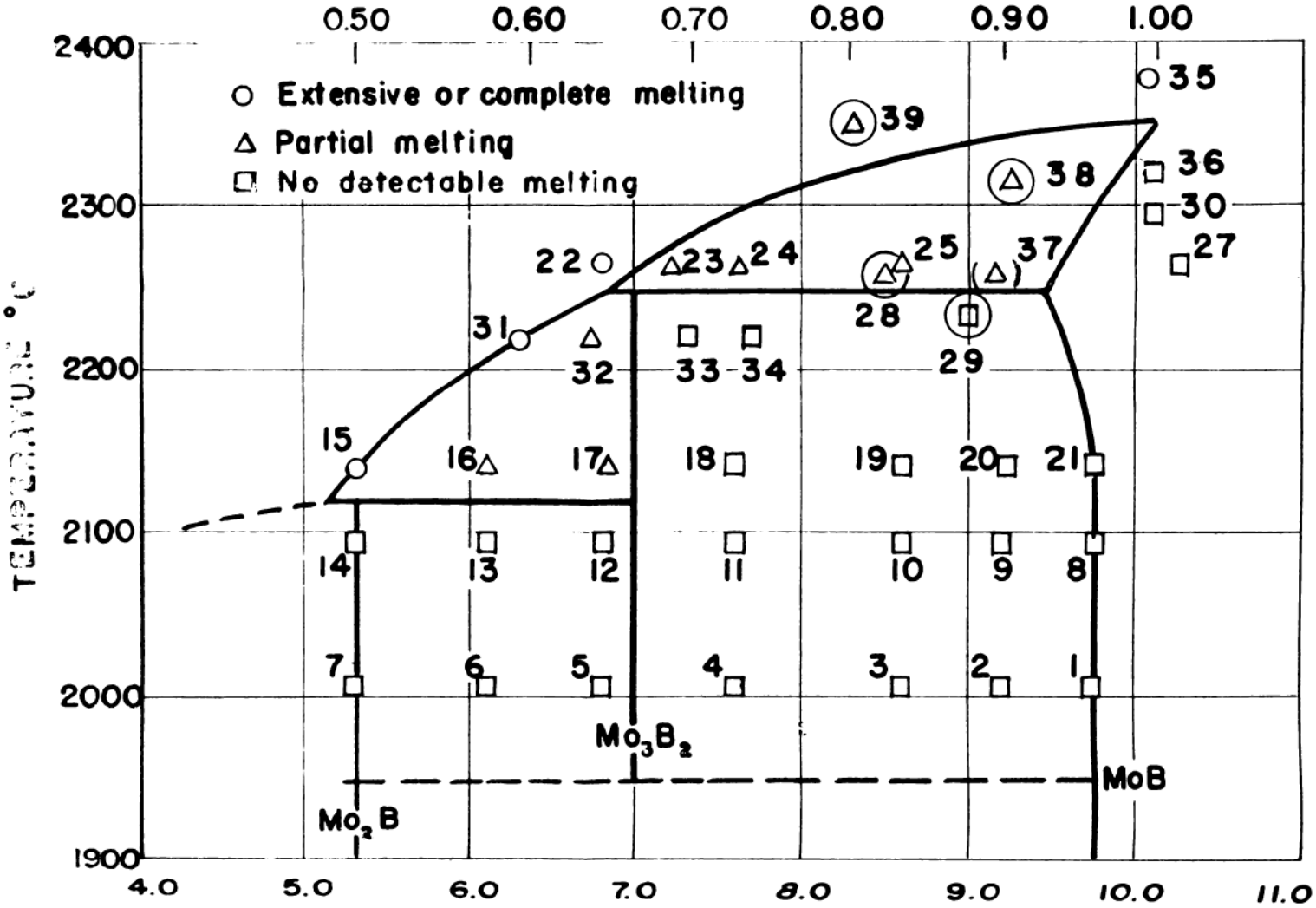
After being heated and cooled the samples were examined visually for melting. Changes from a dull to a bright metallic surface, rounding of edges, and partial or complete collapse of the samples were used to make rough estimates of the degree of melting. X-ray diffraction patterns showed that no reaction with graphite had occurred unless there had been extensive melting. Metallographic examinations were not made.

e. Results

The results of this investigation are shown in the temperature - composition diagram of Figure 1 in a manner similar to that used by

FIGURE 1

PARTIAL Mo-B PHASE DIAGRAM



the authors above. Squares represent samples showing no melting , triangles represent samples showing partial melting, and circles represent samples showing extensive or complete melting. The large circles around squares or triangles indicate experiments carried out in tantalum crucibles. The triangle in the parentheses indicates an observation made on an annular ring of boride which was heated directly by induction. This point masks one of the points, No. 26, obtained in graphite at 2266° C. The individual points are described in Table IV on the following page, and correspond to the numbers appearing on the plot.

3. Discussion

Except for the point No. 39 at 8.3% boron or approximately $MoB_{0.8}$ and 2350° C. obtained from experiments in a tantalum crucible, all data are consistent with the general features of the system as proposed by the previous workers and as drawn here. This discrepancy is not considered serious in view of the fact that the composition of this sample was not well known because of uncertainties in initial composition and changes in composition arising from vaporization.

At the temperatures 2142 and 2221, the appearance of partially melted samples lying to the left of the Mo_3B_2 composition and the appearance of unmelted samples lying to the right of this composition clearly indicate the presence of the compound reported. Rough estimates were made of the extent of melting after the experiment at 2266° C.

Table IV

Summary of Data on the Melting of Boride Samples

Points	Run No.	Remarks
1 - 7	61 a	Multi-cavity cylinder. No melting Temp. = 2008° C.
8 - 14	61 b	Reheat of above. Temp. = 2097° C.
15 - 21	61 c	Fresh charges in individual crucibles. Temp. = 2142° C.
22 - 27	62 a	Point 22 is reheat of No. 17 " 24 " " " " 18 " 25 " " " " 19 " 26 " " " " 20 Points 23 and 27 were fresh charges. Temp. = 2266° C.
28	75 a	$MoB_{0.96}$ heated in Ta for 1 hour at 2261° C. No Ta found spectroscopically. B/Mo = 0.82 after heating.
29	75 b	$MoB_{0.96}$ heated in Ta for 8 min. at 2236° C. Spectroscopic analysis for Ta was negative.
30	77	$MoB_{1.00}$ heated in graphite to 2295° C. for melting point determination.
31 - 34	78	Fresh powder charges heated in individual graphite containers. Temp. 2281° C.
35	79 c	Sample heated in small container, of graphite, to 2373° C.
36	80 b	1/2 inch cylinder heated in graphite to 2325° C.
37	84 c	Annular ring of initial composition 10.3% Boron heated for extended time. Outer layer partially melted and showed B/Mo = 0.90 after heating. Sample heated in graphite support. Temp. = 2265° C.
38 - 39	71 b,c	$MoB_{0.96}$ heated twice in Ta. Compositions estimated on basis of loss of 3 B/Mo in vapor.

and showed that extent of melting decreased with increasing boron content, thus excluding the possibility of a congruently melting compound at Mo_3B_2. There seems, then, to be little doubt concerning the general features of the diagram.

It is apparent from Figure I that the incongruent melting points for Mo_2B and Mo_3B_2 and the melting point of MoB may be set within reasonably narrow limits. It is in these temperatures that the present work differs considerably from that of Steinitz, Binder and Moskowitz. The temperatures are compared in Table V.

Table V

Temperatures (^oC) in the Molybdenum-Boron System

Substance	Phase Change	Previous Work	This Work
Mo_2B	Incongruent melting	2000	2097 - 2142
"	Final melting	2060	2142
Mo_3B_2	Incongruent melting	2070	2236 - 2266
"	Disproportionation	1850	
MoB	Melting	2180	2325 - 2373
MoB_2	Melting	2100	

The Table shows that temperatures differ by about 125 to 175 degrees. Generally, in temperature measurements with an optical pyrometer, errors other than those resulting from gross mismatching of the filament and object tend to make observed temperatures too low. Such is the case, for example, if the object is not a black body, if the pyrometer lenses are dirty, or if absorbing or scattering substances are in the light path.

It is suggested that if the temperatures recorded by earlier workers are too low that they may be so for the following reasons. First, sighting through a gas, as they apparently have done, leads to uncertainties if any convection currents exist in the gas or if any particles remain suspended in the gas. Convection currents may lead to refraction effects and particles screen out light, both tending to give low results. Second, the previous workers sighted into a tube extending into the heated region, the temperature of which may well have been higher than the interior of the tube itself because of the thermal drop across the tube wall. A third factor which may explain in part the difference in temperature is the difference in purities. The samples used by the other workers were claimed to have purities of 96 - 98%, whereas the minimum purity found in this work was 99.0%, and most samples could be expected, on the basis of the assays of the raw materials from which they were made, to be of greater purity.

The complete phase diagram of Figure III and the partial phase diagram of Figure IV in the article of Steinitz, Binder and Moskowitz implies that molybdenum, Mo_2B, Mo_3B_2 and a liquid can exist simultaneously. This is contrary to the phase law, however the first named author subsequently corrected this discrepancy and stated that the eutectic temperature in the Mo - Mo_2B region probably was less than 50° C. below the incongruent melting point of Mo_2B (36). The above named authors also state that Mo_3B_2 is formed by the peritectic

decomposition of Mo_2B, however, the diagram indicates that both Mo_2B and Mo_3B_2 melt incongruently.

Kiessling found that Mo_2B has a narrow range of solid solubility (7), a result with which Brewer and his students were in agreement (16b). It will be assumed in this work that this compound is of definite composition at all temperatures used in this study. The range of solid solubility of Mo_3B_2 is also shown by Steinitz et al as being negligible. According to these authors, the high temperature molybdenum boride is isomorphous with Cr_3B_2 and could therefore be expected to have the same kind of binding as the chromium compound. In view of the fact that Kiessling shows Cr_3B_2 as having a negligible range of homogeneity, (37) it is reasonable to assume that Mo_3B_2 is also of definite composition and such an assumption will be made in this work. The range of composition of MoB is given by the formula $MoB_{0.96-1.06}$ and that of MoB_2 is given by the formula $MoB_{2.14-2.33}$. It will be assumed that the compounds have the indicated ranges of homogeneity at all temperatures.

C. Vaporization Properties and Thermodynamic Stabilities

1. Purpose

The primary object of this investigation was to obtain rate-of-evaporation data from which equilibrium vapor pressures could be calculated and stabilities of the molybdenum borides deduced, and to search for gaseous compounds. The Langmuir equation by means of which vapor pressures can be deduced from experimental data is written for purposes of this investigation as:

$$\alpha_i P_i = 0.02254\, G_i \sqrt{T/M_i}$$

where α_i = accommodation coefficient of species "i"
P_i = partial pressure of species "i" in atmospheres
G_i = rate of evaporation of "i" in gms/cm^2/sec
T = temperature in $^{\circ}$K of the evaporating surface
M_i = molecular or atomic weight of "i"

The method of vapor pressure measurement used in this investigation yields directly only average total rates of loss, that is, $\sum G_i$. It follows, therefore, that auxiliary information pertaining to the identity of the important species and to the accommodation coefficients was required. In addition, the fact that the system is of two components and has more than one solid phase implies that composition changes must occur during vaporization in some of the composition ranges. A knowledge of the important vaporizing processes was therefore also needed to devise experiments, and to interpret data properly; Some of the required information either appears in the literature or may be deduced from literature data, and will be discussed

under the heading "Previous Work". The other information had to be obtained experimentally and is described under the heading "Auxiliary Experiments".

2. Previous Work

Langmuir et al have shown that molybdenum vaporizes to form monatomic gas (42), and that the vapor has an accommodation coefficient of unity. It is possible to calculate the equilibrium constant for the reaction

$$B_2(g) = 2B(g)$$

from spectroscopic data (38,39) and from this to show that for boron pressures to be expected the diatomic boron molecule would be of negligible importance. Brewer has also stated that no gaseous borides except BO, BS, and BF_3 are stable above 2000° K and a total pressure of 10^{-6} atmospheres (6). It is reasonable to assume therefore that only the monatomic elements need be considered in the vaporization processes that occur during the heating of the molybdenum borides to high temperatures.

Glaser has made a study of the systems consisting of a transition metal, carbon and boron (40) and concludes that in general the borides are stable with respect to reaction with graphite except that Mo_2B does react in a carbonaceous atmosphere or with graphite above about 2000° C. (40). This study was useful in selecting graphite as a material of construction. On the basis of studies such as those of Post and on

the basis of other available data, Brewer and Haraldsen have been able to set limits to heats of formation of some of the borides (23).

The Langmuir method for measuring vapor pressures has been applied not only to metals but also to such compounds as NiO (34) and to the study of the equilibrium pressure for the reaction (41):

$$3SrO(s) + W(s) = 2Sr(g) + SrWO_3 :$$

Such studies have indicated that accommodation coefficients are unity. It is reasonable to assume that accommodation coefficients would also be unity in the vaporization processes involving the molybdenum borides.

In summary, it appears that vaporization from heated molybdenum borides should occur to monatomic elements. Accommodation coefficients may be assumed to be unity though data pertaining to the system under study would be desirable.

3. Auxiliary Work

a. Gettering

In the following discussion the term "gettering" refers to the reaction of a vapor with a hot, solid non-volatile reagent such as tantalum and subsequent diffusion into the reagent. A "getter" experiment is considered to be a rate-of-evaporation experiment in which a vacuum is maintained by gettering instead of condensation of a vapor on a cold surface. The "getter factor" is the ratio of the number of atoms of vapor which are "gettered" to the number which are incident on the getter surface.

According to the definitions given above, the condensation coefficient or accommodation coefficient of the vapor being studied must be equal to or greater than the getter factor because sticking, or condensation, must occur if gettering is to occur. Experiments were carried out in which it was possible to show that getter factors for molybdenum and boron on boride surfaces were equal to or of the order of unity and thus to provide evidence justifying the assumption regarding accommodation coefficients made in the preceding section. These experiments will be described because of their applicability to this study and because the gettering technique may be of potential though probably limited value in cases where heating or fabrication difficulties are encountered. The evidence is both qualitative and quantitative.

The qualitative observations consisted of failure to find evidence of attack of surfaces by reflected vapor except where surfaces

had already been heavily attacked. Thus, in a number of experiments in which borides were heated in tantalum or molybdenum containers, it was found that various parts of the assembly cast sharp shadows and surfaces not directly exposed to the vaporizing surface were not attacked.

Two kinds of experiments were carried out which provided information concerning the magnitude of getter factors. The first group of experiments consisted of heatings in which the vapor pressure of boron was measured using a molybdenum crucible as a heater and getter. As a first approximation, the comparison of the vapor pressure measured in that way with that measured by a different method such as the effusion method used by Searcy (44) should give the value of the getter factor for boron on a borided molybdenum surface. An alternate method of comparing results would be to compare heats of vaporization at some reference temperature such as 298° K. Both comparisons are made below and show that the getter factor indicated are unity or nearly unity.

A boron cylinder 1.28 cm in diameter and 0.51 cm in height was used. The history of the sample used prior to the experiments described below is as follows: the sample was prepared from boron batch No. 2 by pressing and sintering at 1700° C. for about 15 minutes. The sample was then heated for approximately 100 minutes at 1525° C. for purposes of making vapor pressure measurements but the run was considered as giving inconclusive results at that time.

Weighings of the sintered sample four days after these experiments, which were carried out during September, 1951, showed that sintered boron cylinders are impervious or nearly impervious to atmospheric attack. The sample was then stored in a dessicator for approximately ten months before being used again.

The sample was heated in a covered 3/4 inch diameter molybdenum crucible. It was supported on a piece of tantalum sheet which had been dented in order to minimize contact. Two heatings were made in a pyrex cell using apparatus No. 2. The first heating, No. 26, was originally intended to be a degassing run but because of the small extent of atmospheric attack the data obtained during the run are included and are used. The data are summarized in Table VI.

The reported temperatures are mean values to which pyrometer and window corrections have been added. The areas shown were the external area of the cylinder as calculated from the dimensions of the cold sample.

Table VI

Summary of Data for Vapor Pressure of Boron by Getter Experiments

	Run 26	Run 27
Time, sec	3600	9000
Temp., °K	2060	2015
Area, cm^2	4.60	4.60
Weight changes, mgms		
sample	-10.8	-11.3
loaded crucible	- 2.4	- 1.3
crucible only	8.5	10.3
Estimated correction due to v.p. of Mo, mgms	0.6	0.7
Corrected gain of crucible	9.1	11.0
P^o_B, Atm., this work	1.7×10^{-7}	8.2×10^{-8}
P^o_B, Atm, Searcy's data	5.9×10^{-8}	2.9×10^{-8}
H^o_{298}, kcal. this work	137	137

The vapor pressure of boron determined in these experiments was calculated on the basis of the corrected gain of the crucible. It was assumed that net loss of the loaded crucible was due to outgassing and loss of molybdenum from the exterior of the crucible. The latter loss was estimated on the basis of the external area of the crucible and data obtained from the paper of Edwards, Johnston and Blackburn (46) and was applied to the crucible gain. The corrected net losses should thus be -1.8 and -0.6 mgm for runs 26 and 27 respectively. These losses are reasonable on the basis of the properties of sintered boron and the assay of the raw material. The calculation of P^o_B was made for each run according to the Langmuir expression on the assumption that the getter factor was unity.

The values of P_B^o found in this work can be compared with those computed from Searcy's heat of vaporization for boron of 140.9 ± 1.4 kcal and from Brewer's free energy functions (43,44). It can be seen that the values found in this work are higher than those computed from the above data.

The values of ΔF^o were combined with Brewer's free energy functions to obtain the indicated values of ΔH_{298}^o in the usual way.

The data summarized in the table above indicate that the getter factor is apparently higher than unity, however it is believed that the data found in this work agrees within experimental limits with that given by Searcy so that it may be concluded that the getter factor of boron on a borided surface is unity or nearly unity. Since "sticking", or condensation is a necessary process in gettering, it follows that the accommodation coefficient of boron on a boride is unity or approaches unity. There is no reason to believe that the accommodation coefficient of molybdenum vapor should not also approach or equal unity on one of its compounds.

A second group of experiments was carried out the objectives of which were (a) to evaluate getter factors, (b) to determine whether or not MoB has a constant subliming composition and (c) to measure rates of evaporation in order to determine stabilities if such a composition were found to exist. The experiments culminated in the melting of the sample, a fact which was shown on the basis of weight loss - composition change data to have been due to preferential loss of boron. Sufficient

data were taken however to show that getter factors must be of the order of unity.

A boride cylinder of approximately 12 mm diameter was prepared from molybdenum batch No. 1 and boron batch No. 3 in a manner described earlier. The initial composition of the sample was 9.6% boron and 90.2% molybdenum or $MoB_{0.96}$

Heatings were carried out in apparatus No. 2 equipped with a quartz cell. The heating arrangement is shown in the sketch of Figure II and employed a tantalum heating element which heated a tantalum spinneret and its contents by radiation. The spinneret was dented on the side and bottom in order to minimize contact with the sample.

The data taken during the runs on a single cylinder are summarized in Table VII. Run 71 a, of 8 minutes duration at 2200° C. was a sintering and outgassing run on which no data were taken. Runs 71 b and c were intended to cause a weight loss of about 10% in order to permit the sample to reach its constant subliming composition, if such a composition exists. Runs 72 a and b were made to outgas a new spinneret in preparation for run 73 and provides information by means of which outgassing corrections could be applied to weight change data taken on the previous runs. Run 73 was intended to provide data for evaluation of getter factors, and weight loss data for calculation of equilibrium pressures but proved to be abortive in that the sample melted. The melting of the sample during run 73

led to the conclusion that composition changes occurred, a conclusion which was subsequently confirmed by making composition change - weight loss determinations.

The basis for making the getter factor determination consisted of comparing the weight of vapor gettered with the weight incident on the gettering surface. It was assumed that the net weight loss suffered by the spinneret and contents took place by virtue of effusion through the orifice in the spinneret cover and that the weight of vapor incident on the under side of the cover could be measured by that loss. The assumption was also made, as a first approximation, that vapor would not be reflected from the under side of the heater cover, an assumption which appeared justified in view of the fact that there was no evidence of vapor attack on the top of the spinneret cover. That is, had the effusing vapor been reflected from the hot heater top, there should have been evidence of some attack by vapor which had been reflected on to the top of the spinneret cover. The absence of such attack is taken as qualitative evidence that getter factors were nearly unity.

The fraction of vapor that was gettered could be determined by comparing the weight gain of the spinneret top per unit area with the rate of incidence per unit area as measured above. The assumption that the rate of incidence per unit area was constant over the underside of the cover was made but it was probably not precisely correct to do so.

FIGURE 2

HEATING ASSEMBLY FOR GETTER FACTOR EVALUATION

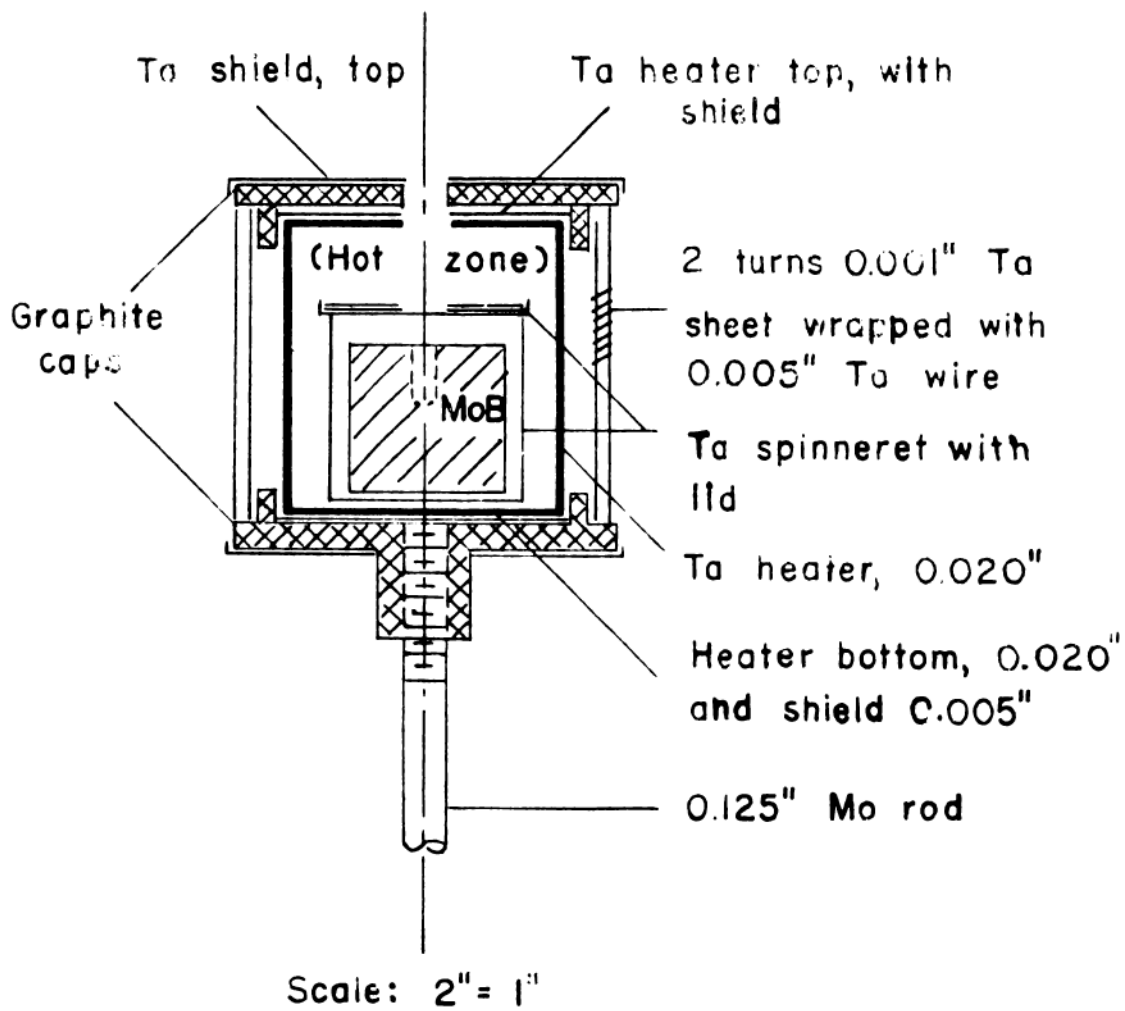


FIGURE 2

HEATING ASSEMBLY FOR GETTER FACTOR EVALUATION

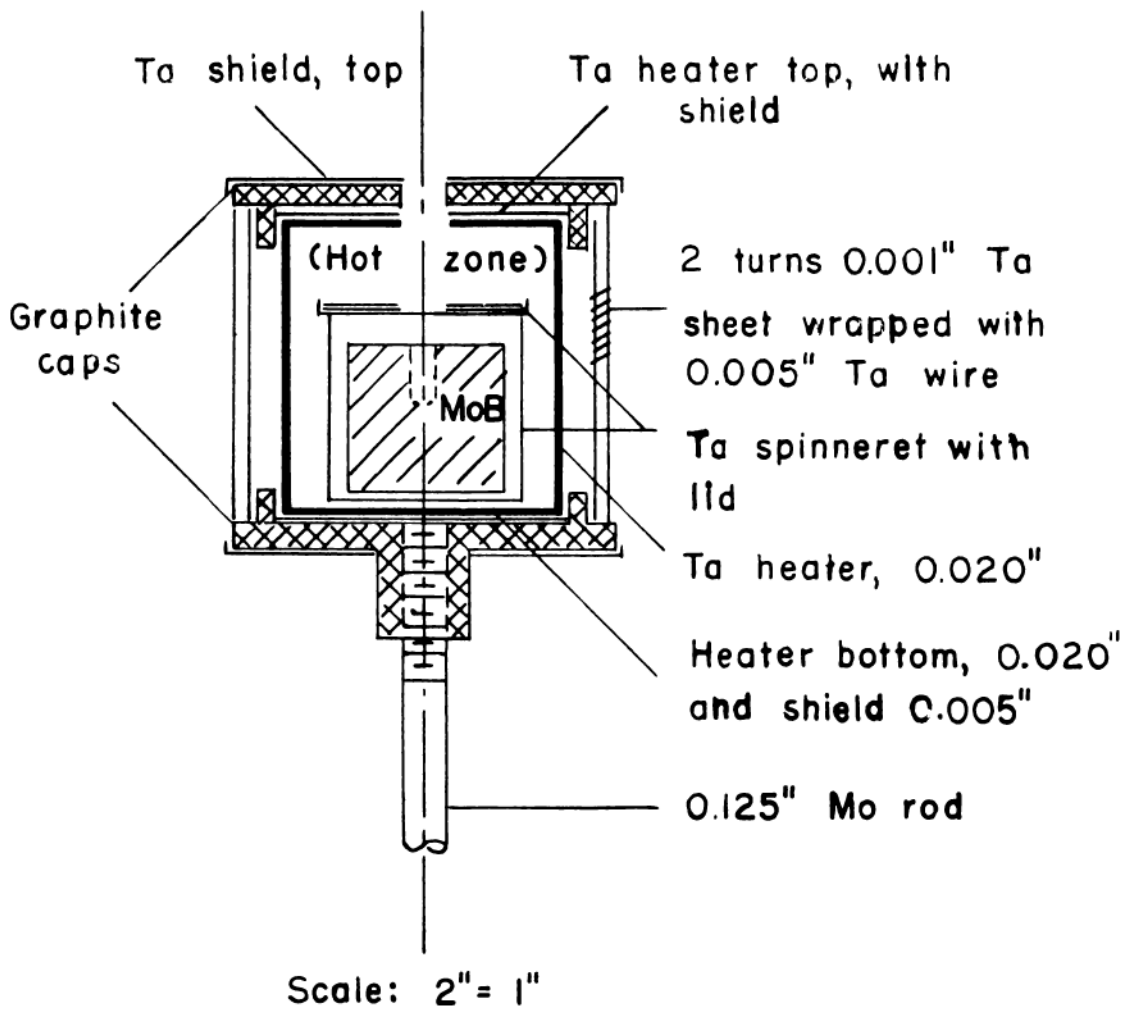


Table VII

Summary of Data for Getter-Factor Experiments

Run	71 a	71 b	71 c
Time, sec	480	3600	3600
Temp. °C.	2200	2320	2345
Sample dimensions		D. x H	
init'l, cm		1.18 x 0.93	1.12 x 0.91
final "		1.12 x 0.91	1.08 x 0.86
Wt. of sample, gms			
initial		5.9808	5.7903
final		5.7903	5.5454
loss		0.1905	0.2449
Wt. of spinneret, (loaded)			
initial, gms		10.0887	10.4045
final, gms		10.0666	10.3800
net loss, gms		0.0221	0.0245
spinneret cover gain, gms		broken	0.0433
orifice diam, cm		0.45	0.45
reaction area diam, cm		1.40	1.40

Run (blank)	72 a	72 b
time, sec.	3600	3600
temp. °C.	2350	2270
spinneret loss		
gms. without lid	0.0053	0.0009

The getter factor may be computed in terms of weight changes and diameters as shown below for run 71 c.

$$\text{Getter factor} = \frac{43.3}{(1.40^2 - 0.45^2)} \Big/ \frac{42.5}{(0.45)^2} = 0.20$$

where the numerator is proportional to the rate of gettering and the denominator is proportional to the rate of incidence.

It may be seen from the manner in which the experiment was conducted that getter factors would be very sensitive to any error that tended to give high rates of incidence. Such errors could result from loss of impurities such as iron from the sample itself, or from outgassing of the tantalum container. That such errors actually did occur was shown by the fact that approximately 2 mgms of iron was found in the condensate formed on the quartz cell wall and by the data given for the "blank" runs. Recalculation of the getter factor after applying an estimated correction of 4.5 mgms to the net loss gives a factor of 0.25. It is worth noting that the sample used in run 71 c was partially melted with the liquid probably coating the outside. The composition change in similar samples as noted in section C, part 2, indicated that the escaping mole ratio was approximately 3 B per Mo.

In the following discussion it is assumed that the boron and molybdenum vapor arising from the sample react with the tantalum to form a layer of tantalum-boron-molybdenum alloy above which the

partial pressures of molybdenum and boron are smaller than the partial pressures under investigation. If the concentration of the condensed, or gettered, vapor increases in the alloy layer as vaporization continues during an experiment, then the partial pressure of the boron and molybdenum might be expected to increase with consequent "back" vaporization, unless diffusion of the gettered vapor into the getter is sufficiently rapid to maintain a low concentration. This effect would appear to be particularly applicable to molybdenum and might account for the low observed getter factor.

It is apparent, nevertheless, that a very substantial fraction of the vapor must have condensed on the alloy surface in the manner postulated by Langmuir and that observed low getter factors are explainable in terms that are not inconsistent with the assumption that accommodation coefficients are unity or nearly unity.

b. Vaporization Processes

The experimental work on which the following discussion is based extended throughout the entire period of this investigation, however, it is convenient, before going on to describe the determination of the stabilities of the individual borides, to discuss the subject of vaporization processes at this point.

The means by which the general pattern of behavior was determined consisted of observations of composition changes produced when borides were heated in a vacuum and comparisons of rates of loss from borides with that from molybdenum metal. The important

procedures consisted of the analytical methods for boron and molybdenum, and the x-ray identification of solid phases. Of the observations which led to the conclusions to be discussed below, those which were most free of objections were made on runs to be described in connection with the determinations of stabilities and therefore no detailed description of those experiments will be given here. In general, however, the methods of preparation of samples and heating and the procedures used have already been indicated previously.

Results of observations have led to the conclusion that there is no constant subliming composition in the Mo - B system, and no important gaseous boride is of sufficient stability exists to be considered. It was also found that if a given higher boride such as MoB_2 were heated in vacuum, the preferential loss of boron causes the formation of a lower boride through which boron diffuses. The general reaction to be considered is thus

$$MoB_x(s) = Mo(g) + xB(g)$$

where MoB_x represents the lower boride constituting the surface layer. Because vaporization occurs from a single solid phase surface having two components, it follows that the partial pressures of molybdenum and boron are not fixed, but must be used to calculate an equilibrium constant, $K_p = P_{Mo} \times P_B^x$. The system appears to be very much like the Al - Al_2O_3 system studied by Brewer and Searcy (45), but is simpler.

The experiments by which the above conclusions were reached are described briefly below. Mixtures of MoB and MoB_2 having compositions ranging from $MoB_{1.0}$ to $MoB_{2.2}$ were suspended within individual molybdenum cylinders to isolate samples from one another and heated in a molybdenum crucible. Heatings of about one hour duration in the temperature range 1825° C. to 1900° C. were conducted. X-ray examinations of the starting material before the runs and similar examinations of the samples after the runs showed clearly the presence of an outer layer of MoB and an inner core of MoB_2 or MoB_2 together with MoB, depending on the initial composition.

Two preliminary getter experiments and one conventional Langmuir experiment showed that boron is lost preferentially from MoB as determined by weight loss and corresponding composition change data. These experiments are listed below together with pertinent weight loss and composition data.

Run 76 a. A sample of initial weight 0.8680 gm lost 0.0125 gm and the weight percent boron decreased from 8.5 to 8.3%, in a getter experiment.

Run 76 b. A sample of initial weight 2.3023 gms lost 0.0275 gm and the weight percent boron decreased from 9.0 to 8.9% in a getter experiment.

Run 84 c. A solid cylinder of MoB weighing 23.7441 gms initially underwent a loss of 0.2308 gms and

a corresponding change of boron content from 9.0 to 8.9 weight-percent.

The information above thus indicates that MoB loses boron preferentially.

Cylinders of MoB and of Mo_2B were heated by induction in a manner to be described in the sections following this and were found to have outer layers of Mo_2B and Mo respectively after heating. These outer layers were persistent with heating so that the possibility of composition changes resulting from adsorbed or dissolved impurities such as oxygen was precluded.

That no important gaseous species exists could be shown by comparison of rates of loss from the Mo_2B cylinder with the rate of loss from Mo. If a metal layer were formed on the surface of the Mo_2B cylinder, the rate of loss of metal should be equal to that corresponding to the vapor pressure of the metal itself. A further contribution to the rate of loss should occur by virtue of vaporizing boron. If a gaseous boride were important, the total measured rate of loss should be greater than that due to the vaporization of the elements alone. Within experimental limits this was not found to be the case so that the possibility of any important gaseous boride is eliminated.

4. Stability of Mo_2B

The stability of Mo_2B was studied by use of two reactions:

(1) $Mo_2B(s) = 2Mo(g)+B(g)$

(2) $Mo_2B(s) = 2Mo(s)+B(g)$

Process (1) could be utilized by heating a cylinder of $MoB_{0.96}$ in vacuum so that the preferential loss of boron left an outer layer of Mo_2B through which boron diffused from the interior as described in a previous section of this report. Analysis of the sublimate for molybdenum and boron together with rate-of-evaporation data made possible the determination of K_p for the reaction. The free energy changes calculated from K_p were then used with free energy functions to compute ΔH^0_{298} of formation for the solid.

Six cylindrical samples approximately 19 mm in diameter and 16 1/2 mm high were prepared from molybdenum batch No. 1 and boron batch No. 5. The preparation of the boride, the fabrication of the samples and the purities of samples as prepared for rate-of-evaporation experiments have already been discussed. Of the six cylinders, three were used, each of which was subjected to three runs.

The apparatus No. 2 with quartz cells was employed for the heatings. The equipment and details of the heating arrangement used are given elsewhere (28). The heating arrangement was much the same as that shown in Figure II except that the tantalum heater was replaced by the sample itself and the top and bottom tantalum sheet used for radiation shields next to the heated element were replaced by graphite discs turned from spectroscopic grade graphite rod. The graphite was used in place of tantalum to avoid warping that would result from reaction of the metal and vapor.

Before rate-of-evaporation experiments were carried out, one run, designated run 84 c, was made to obtain assurance that no significant errors would occur as a result of temperature gradients. Another experiment, designated run No. 85 b, was also made to obtain assurance that temperature readings would be made by sighting into a blackbody hole.

For run 84 c, a 1/16 inch diameter hole was drilled longitudinally down the center of one sample cylinder to a depth of 1/2 inch and a similar hole was drilled near the cylinder wall approximately 9/32 inch from the center. The cylinder was then heated to about 2260° C. in line No. 2 in a typical heating arrangement and temperature readings were taken on both holes. Differences of 15° C. were noted. Because of the nearness of the outer hole to the outer layer of boride within which heating took place by induction, it was estimated that the temperature of the wall would be no more than 5 degrees higher than that read in the outer hole. The error could be expected to be smaller at lower temperatures. Since temperature readings could be reproduced to within a range of only about 10 degrees at 2000° C or higher, it was assumed that errors due to temperature gradients would be negligible.

For the second experiment, run No. 85 b, three holes 1/16 inch in diameter were drilled 3/8, 1/2 and 5/8 inch deep on a 9/16 inch diameter circle and the sample was then heated as above to 1900° C. Three observers took readings on each hole and the readings were

found to fall within the range 1900 to 1909° C. It was therefore concluded that a hole at least six times as deep as its diameter in a boride cylinder should be a blackbody.

After the preliminary tests described above were conducted, the rate-of-evaporation experiments were carried out. After evacuation of the system, power was applied after first setting the gap at a point estimated on the basis of past experience which would produce a desired temperature. Temperature readings were taken at intervals of about one minute during the warm-up period and then at increasingly longer intervals as the temperature leveled off. It was not possible to use the available automatic temperature control circuits because the introduction of a variometer resulted in excessive lowering of the available temperature. The temperature was therefore controlled within a range of about twenty degrees by means of a galvanized bucket filled with water which was placed between the radio-frequency leads to the work coil. Movement of the leads with respect to the bucket could produce temperature changes of about 25 degrees.

The data taken for the experiments consisted of the following: weights of the sample and parts of the heating assembly before and after heating, dimensions of the sample prior to the heatings, temperature-time data, and spectroscopic analyses of the tantalum shields for boron and molybdenum. In addition to the data taken above, optical windows were calibrated a number of times during the experimental work

to make sure that no significant absorption correction changes occurred. A sample was also examined prior to a series of runs by x-ray diffraction and was found to have an all-Mo_2B surface. All samples were examined after their series of heatings in a similar manner to make sure that evaporation took place from Mo_2B surfaces during all runs.

The data taken during this work is summarized in Table VIII, and will be discussed below. The net loss is the difference in weight of the sample and end shields before and after the runs. It was assumed that no net loss from the ends of the sample occurred. The shield gain was the difference in weight of the shield before and after the runs and is believed to be the significant weight change because of "leakage" of vapor past the slots in the graphite caps, loss through the holes through which temperature readings were taken, and evolution of impurities against which the shield seemed to discriminate. The initial area of the sample was calculated from the diameter and height of the cold sample prior to the run. It may be seen that an additional shrinkage in area of 1 to 2% occurred per run.

The temperatures and times of the runs were determined from plots of temperature versus time. Mean temperatures were evaluated visually with the aid of a plastic strip on which a straight line had been scribed, and were estimated to be correct to $\pm$ 8° C. The true temperatures are, of course, subject to an uncertainty of $\pm$ 20° C. The usual window and pyrometer corrections were applied to the mean

Table VIII

Summary of Data on the Equilibrium $Mo_2B(s)$ $2Mo(g)$ $B(g)$

Cylinder No.	85			86			87		
Run No.	e	f	h	e	f	h	e	f	h
Net Loss, mgms	16.3	46.9	43.8	19.2	20.9	33.2	32.6	49.5	44.1
Shield Gain, mgms	7.4	40.7	40.7	13.3	18.1	29.2	26.9	43.3	39.3
Initial Area, cm^2	8.62	8.49	7.99	8.40	8.30	8.22	8.63	8.41	8.16
Mean Temp., °K	2244	2377	2374	2234	2237	2332	2381	2365	2311
Time, Seconds	7700	5800	6420	12,840	19,800	7620	7080	14,400	15,000
Vapor Composition, Wt.-Fraction Boron		0.16	0.18	0.17	0.17	0.19	0.14	0.21	0.24
P_B, Atm.		4.42×10^{-8}	4.76×10^{-8}	6.71×10^{-9}	6.05×10^{-9}	2.92×10^{-8}	2.03×10^{-8}	2.48×10^{-8}	2.54×10^{-8}
P_{Mo}, Atm.		7.77×10^{-8}	7.27×10^{-8}	1.11×10^{-8}	9.98×10^{-9}	4.18×10^{-8}	4.20×10^{-8}	3.13×10^{-8}	2.70×10^{-8}
$K_p = (P_B)\ (P_{Mo})^2$		2.66×10^{-22}	2.52×10^{-22}	8.26×10^{-25}	6.03×10^{-25}	5.10×10^{-23}	3.58×10^{-23}	2.43×10^{-23}	1.85×10^{-23}
$-\text{Log } K_p$		21.575	21.599	24.083	24.226	22.296	22.450	22.614	22.737

temperature and the results are recorded in the Table. The effective starting time of the run was estimated visually. In view of the fact that the entire warm-up period did not exceed 8% of the total heating time in any case and it is reasonable to assume that virtually no vaporization occurred during the first few minutes of the run, the error in time as estimated above is believed to be no greater than 2 or 3%.

The analytical procedures for the determination of the vapor composition were described earlier. Although these determinations were subject to considerable uncertainties, the effect of these uncertainties on calculated values of stabilities is not large as can be seen by considering the data for run 87 e as an example. In this run, the experimental $K_p = 3.58 \times 10^{-23}$ and the sublimate was found to have a weight fraction of boron of 0.14. Recalculation on the basis of the maximum weight fraction of boron found, namely 0.24 gave a value of $K_p = 2.44 \times 10^{-23}$. The corresponding negative logarithms of the K_p values are 22.450 and 22.612 for a weight fraction of boron of 0.14 and 0.24 respectively. The equilibrium constants were calculated on the basis of shield gains for reasons indicated above. It may be seen that shield gains are approximately 15% lower than net losses. Even though the total difference were attributed to loss of boron only, it is apparent from the above that no significant error would result.

The partial pressures of boron and molybdenum were calculated

using Langmuir's equation in which the accommodation coefficient was taken as unity. The equilibrium constant needs no comment. The negative of the logarithm of K_p for each determination is shown for convenience in later calculations of ΔH°_{298}. A plot of Log K_p vs 1/T is given in Figure III in which the slope of the line is drawn to correspond to a heat of 478.3 kcal, the calculation of which will be described later.

Care was taken to minimize error due to atmospheric attack. Thus, samples were exposed to the atmosphere for the minimum time possible between runs. In the case of sample 85, about one month delay occurred between run 85 f and 85 h. Accordingly the sample was outgassed in run 85 g immediately prior to run 85 h. Runs on samples 86 and 87 were made consecutively, the samples being removed from the vacuum line only long enough to permit making the necessary weighings and measurements.

Run 85 e was not used on the grounds of low weight loss and excessive difference between net loss and shield gain. The low weight loss resulted in a concentration of sublimate in tantalum which was beyond that for which calibration curves were considered useable. The large relative difference between the weight changes indicated above suggested that excessive errors might be expected because of possible oxidation.

In run 85 f, observed temperature readings varied more than twenty degrees; that is, readings decreased with increasing time.

The effect was attributed to the fact that in this run, the window was exposed to the sample for a relatively large fraction of the total time, that is, about 10 to 15%. The window correction applied was therefore based on calibrations made before and after the run. In the following runs, care was taken to make readings with a minimum of "exposure" time, and frequency of readings was reduced, with the result that no significant change in absorption corrections were subsequently found.

In the case of runs 86 e and f, the same tantalum shield was used for both runs in order to maintain a sufficiently high sublimate concentration in the tantalum to make possible the use of calibration curves used for analysis. The vapor composition shown for these runs is the average for the two.

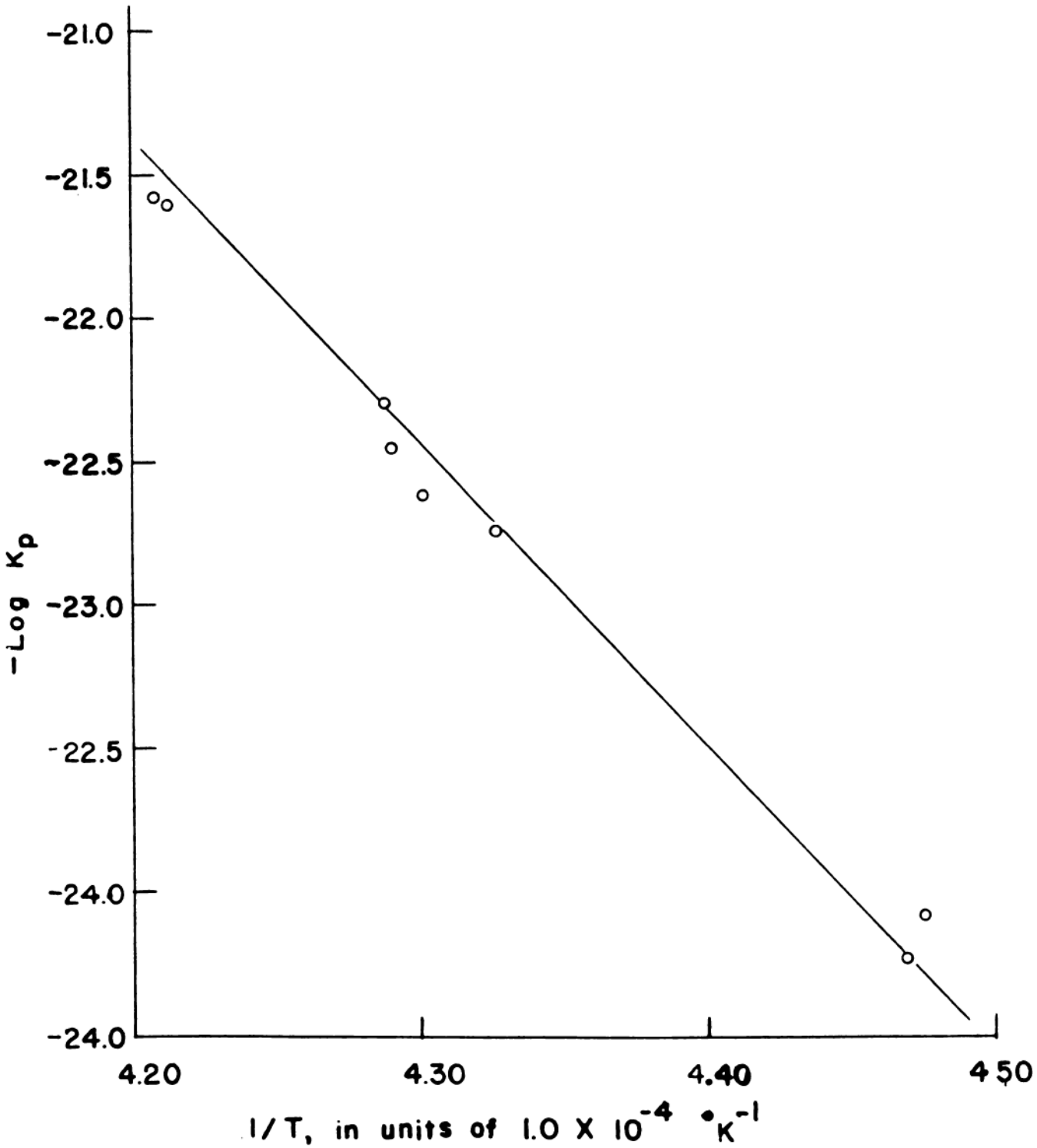
The equilibrium constant data summarized in Table VIII may be used in a number of ways to find a heat of reaction. Thus, a heat could be found from the slope of the curve of Figure III according to the integrated from of the Clausius-Clapeyron equation

$$\ln K_p = -\Delta H/RT + I$$

The use of this method however was not feasible in this case because of the relatively small temperature interval used for the experiments, and the relatively large uncertainties in temperature measurements. The relatively large uncertainties in K_p resulting from analytical limitations are also important in this case.

FIGURE 3

LOG K_p vs 1/T



A second method consists in the use of entropies, or estimated entropies, to calculate heats according to the equation

$$\Delta H = \Delta F + T \Delta S$$

The free energy changes at temperature T could be computed in the usual manner from the equilibrium constants. In the absence of measured high temperature entropies, one would be required to estimate entropy changes. Latimer has discussed the estimation of entropies of elements in compounds (47), but use of his method required information regarding oxidation number, a quantity having little meaning in the case of borides of the transition metals. An estimation of the entropy of boron in borides, based on data for carbides and nitrides, leads to the value -3 e.u. Entropies of various molybdenum borides were calculated according to Latimer's data and are compared with those computed from NBS data (48) assuming no entropy change of formation.

Table IX

Comparison of Estimates of Entropies of Borides

Boride	Based on Latimer	Based on NBS Tables, $\Delta S(f) = 0$
Mo_2B	21.6	15.22
Mo_3B_2	30.9	23.61
MoB	9.3	8.39
$MoB_{2.35}$	5.3	10.47

A third method of finding a heat of reaction is to use free energy functions. The free energy of an element or a compound may be computed from thermal data in the case of solids or may be calculated for gases from data derived wholly from spectroscopic data. Calculations pertaining to equilibria are conveniently made with the use of such functions and heats of reaction at some reference temperature, usually 0 °K or 298° K and thermal data are very conveniently summarized in the form of such quantities. For these reasons, thermodynamic information is commonly reported in that form and the following discussion will be based on the use of free energy functions.

Free energy functions for solid compounds will be assumed to be equal to the sum of the free energy functions of the constituent elements. This is equivalent to assuming that ΔS and ΔCp of formation are zero. In the case of vaporization reactions the uncertainty introduced by this approximation is small relative to the total change in free energy function because of the small values of this function for solids. For convenience, values of $-(\Delta F^{\circ} - \Delta H^{\circ}_{298})/T$ at various temperatures for vaporization of molybdenum and boron are listed in Table X and calculations in this and following discussions are based on those values.

The data for molybdenum are taken from Edwards, Johnston and Blackburn's paper on the vapor pressure of molybdenum (46) and are corrected to a reference temperature of 298° K using a value of 394

Table X

Summary of Free Energy Function Data

For Mo(s) = Mo(g)

Temp. °K	$-(\Delta F^\circ - \Delta H^\circ_0)/T$	$(\Delta H^\circ_{298} - \Delta H^\circ_0)/T$	$-(\Delta F^\circ - \Delta H^\circ_{298})/T$
2155	34.18	0.18	34.36
2185	34.07	0.18	34.25
2231	33.92	0.18	34.10
2240	33.90	0.18	34.08
2260	33.83	0.17	34.00
2300	33.70	0.17	33.97
2397	33.37	0.16	33.53
2434	33.24	0.16	33.40
2462	33.15	0.16	33.31

For B(s) = B(g)

Temp. °K	500	1000	1500	2000	(2500)
$-(\Delta F^\circ - \Delta H^\circ_{298})/T$	35.1	35.6	35.6	35.4	(35.0)

calories for $\Delta H^{\circ}_{298} - \Delta H^{\circ}_{0}$ as taken from Brewer's tables and Simon and Zeidler's thermal data for the solid metal (49). The data for boron are taken entirely from Brewer's tables of thermodynamic functions for the elements(45). The value in parentheses is an extrapolated one but, because of the slow change in free energy function differences with temperature, should lead to negligible error.

Computations of ΔH°_{298} for the process

$$Mo_2B(s) = 2Mo(g) + B(g)$$

are tabulated on the following page. Calculation of ΔH°_{298} is based on the equation

$$\Delta H^{\circ}_{298}/T = -(\Delta F^{\circ} - \Delta H^{\circ}_{298})/T + \Delta F^{\circ}/T$$

The table lists values of the heat of reaction for each run in the right hand column. It is seen that the average value of ΔH°_{298} is 478.3 kcal. Using Searcy's heat of vaporization of boron and Edwards, Johnston and Blackburn's value for molybdenum after correction to 298 $^{\circ}K$, it is found that the heat of formation of $Mo_2B(s)$ from the solid elements is -25.5 kcal.

It should be pointed out that the experimental results obtained as described above pertain to a sample of $Mo_2B(s)$ which was effectively heated in an excess of B(g) which was derived from the interior of the samples. It is possible to deduce the nature of the changes which would occur if pure Mo_2B were heated in a vacuum from the data obtained and from a knowledge of vapor pressures of the elements.

Table XI

Summary of Computations of Heat of Vaporization of Mo_2B

Run and Temp. °K	$-(\Delta F - \Delta H^{\circ}_{298})/T$ in cal/deg.	$\Delta F^{\circ}/T$ cal/deg.	$\Delta H^{\circ}_{298}/T$ cal/deg.	ΔH°_{298} in kcal
85 f (2377)	102.3	98.8	201.1	478.0
85 h (2374)	102.3	98.9	201.2	477.6
86 e (2234)	103.4	110.3	213.7	477.4
86 f (2237)	103.4	111.0	214.4	479.6
86 g (2332)	102.7	102.1	204.8	477.6
87 e (2331)	102.7	102.8	205.5	479.0
87 f (2325)	102.7	103.6	206.3	479.6
87 g (2311)	102.7	104.1	206.8	477.9
			avg =	478.3

$$\text{P.E.} = 0.6745 \sqrt{\frac{\Sigma\Delta^2}{n(n-1)}} = 0.2 \text{ Kcal.}$$

First, let it be assumed that pure Mo_2B were to volatilize only according to the process

$$Mo_2B(s) = 2Mo(g) + B(g),$$

that is, the above process is assumed to be the only one that would occur. It follows, then, that for each atom of boron vaporizing, two atoms of molybdenum must vaporize. Because of the fact that rates of volatilization into a vacuum are dependent on atomic weights as well as equilibrium pressures, $P_B \neq 1/2\ P_{Mo}$ in this case, as would be true in an equilibrium type experiment. That this is true may be seen from Langmuir's equation. Noting that the experimental conditions require that $n_B = 1/2\ n_{Mo}$, where the n's are rates of evaporation in gram-atoms/cm^2/sec one sees that the ratio of P_B/P_{Mo} is given by

$$\frac{P_B}{P_{Mo}} = \frac{0.02254(1/2n_{Mo})\sqrt{TM_B}}{0.02254(n_{Mo})\sqrt{TM_{Mo}}}$$

Substitution of the appropriate atomic weights shows that in the postulated case, $P_B = 1/5.95\ P_{Mo}$. The rate of mass transfer would differ in the Langmuir and equilibrium experiments for the same reason. The free energy change for the process is given by the expression $\Delta F^\circ = -RT \ln (P_{Mo})^2(P_B)$, where the product $(P_{Mo})^2(P_B)$ may be recognized as the equilibrium constant for the process.

Next, let it be assumed that the stability of the solid, and therefore the free energy of the above process, can be decreased.

It follows therefore that the pressures must become greater but that they must maintain a constant ratio so long as the assumed process occurs exclusively. If, in the hypothetical case, the stability were allowed to continue decreasing, then because P^{o}_{Mo} is less than P^{o}_{B}, the partial pressure of the metal vapor would ultimately reach its limiting value, namely, P^{o}_{Mo} and at that point, solid molybdenum should just start to appear. As the decrease of stability is allowed to continue, the pressure of the metal vapor may not increase, but that of the boron will. In conventional practice, the partial pressure of boron, in the situation now prevailing, would be considered as being the equilibrium constant for the reaction

$$Mo_2B(s) = 2Mo(s) + B(g).$$

To determine the equilibrium pressure for the above reaction, one need only divide the equilibrium constant for the initial case by $P^{o\,2}_{Mo}$. If it were found that the resulting quotient were numerically greater than 0.168 P^{o}_{Mo}, then it follows that $Mo_2B(s)$ should lose boron at a rate greater than 1/2 that of molybdenum and that the boride should leave a residue of free metal on being heated. By similar reasoning, it is possible to set an upper or lower limit to stability of Mo_2B according to whether molybdenum does or does not appear when pure Mo_2B is heated in a vacuum. Similar conclusions could be drawn for the equilibrium case though the numerical values would differ because of the atomic weight effect.

Calculations based on the reasoning above and the data previously described indicate that Mo_2B is not a constant subliming compound. These calculations will be shown below. For future convenience, the temperature chosen will be 2200° K. From the data of Table X, the value of $-(\Delta F^\circ - \Delta H^\circ_{298})/T$ for the vaporization of Mo_2B is found to be 104.6. Therefore,

$$-\Delta F^\circ/T = 104.6 - 478{,}300/2200 = -112.8$$

$$-\Delta F^\circ/T = 4.58 \text{ Log } K_p = -112.8$$

$$K_p = 2.4 \times 10^{-25}$$

From the data of Edwards, Johnston and Blackburn, P°_{Mo} is found to be 9.4×10^{-9} atmospheres. P_B for the reaction involving the free metal is therefore

$$P_B = 2.4 \times 10^{-25}/(9.4 \times 10^{-9})^2 = 2.7 \times 10^{-9}$$

atmospheres. This is greater than $1/5.95\ P^\circ_{Mo}$ so that Mo_2B should not be a constant subliming compound when heated in vacuum. A verification of this conclusion is described in the following experimental work, in which reaction (2) was studied.

For the purpose of studying the process

$$Mo_2B(s) = 2Mo(s) + B(g)$$

a cylinder of Mo_2B was prepared from molybdenum batch No. 2 and boron batch No. 6 and is designated here as sample No. 93. The method of preparation and of fabrication were the same as those used for previous work.

The sample was heated in apparatus No. 2 using quartz cells and the same kind of heating arrangement as was used for work with the Mo_2B - MoB cylinders described above.

The cylinder was subjected to a series of heatings during which composition changes occurring at the surface were determined by x-ray diffraction examination. In addition to surface examinations, weight loss and gain data and time vs. temperature data were taken. The runs and changes in surface composition are most conveniently described in tabular form.

Table XII

Data on Changes of Surface Composition of a Mo_2B Sample

Run	Heating Conditions	Wt. loss mgms	Composition of the surface
93 b	3/4 hr. at 1815° C.	45	Mo_2B with trace of MoB before heating. Mo on surface after.
	Surface ground after run to expose Mo_2B		
93 c	50 min. at 2000-2050° C.	40	Mo principally, trace of Mo_2B
	Surface ground after run to expose Mo_2B		
93 d	30 min. at 2000-2035° C.	14.5	Mo with minor amount of Mo_2B
	Surface not ground, heating continued		
93 e	2 hrs. at 2075	60	Mo only

Runs 93 b and c may be regarded as degassing runs though the tendency of the sample to lose boron preferentially is indicated by the x-ray observations. However because the sample was not ground between runs 93 d and 93 e and thus no oxides were introduced and because run 93 e was carried out for a sufficiently long time and at a high temperature such that interference by extraneous processes was excluded, it is believed that this pair of runs demonstrates clearly that Mo_2B is not a constant subliming compound when heated in a Langmuir experiment.

A second group of runs were carried out on the sample in order to make quantitative determinations of rates of evaporation from a Mo - Mo_2B surface. The sample was ground to expose Mo_2B, subjected to a degassing run and then to a data run. The sample was examined after each data run to make sure of the presence of Mo_2B. No examination by use of x-rays was made prior to the data runs since it is reasonable to assume that Mo_2B and Mo would be present during the run if they were present at the end. Runs 93 d and 93 e are listed with the second group because approximate data were available. The data for this group of experiments are given in Table XIII.

The net loss, shield gain, temperature, area and time of heating in Table XIII need no discussion since the procedure used in these experiments was the same as that used before. The vapor pressure of molybdenum and the weight loss due to volatilization of the free

Table XIII

Summary of Data on the Equilibrium

$Mo_2B(s) = 2Mo(s) + B(g)$

Run	93 d	93 e	93 g	93 i
Net loss, mgms	12.7	45.3	6.1	4.3
Shield gain, "	6.3	39.7	5.2	3.5
Temp. ^{o}K	2310	2350	2260	2245
Area, cm^2	7.7	7.6	7.2	7.1
Time, sec	1600	7260	3600	2940
P^{o}_{Mo} Atm.	4.32×10^{-8}	7.22×10^{-8}	2.80×10^{-8}	1.82×10^{-8}
Calculated loss of Mo, mgms	4.9	35.9	5.2	3.5
Measured P_B Atm	3.8×10^{-8}	2.3×10^{-8}	-	-
$K_p = P_{Mo}{}^2 \times P_B$	1.8×10^{-23}	1.1×10^{-22}	1.8×10^{-24}	8.7×10^{-25}
$P_B = K_p / P^{o2}_{Mo}$	1.0×10^{-8}	2.1×10^{-8}	3.7×10^{-9}	2.6×10^{-9}
P_B / P^{o}_{Mo}	0.23	0.29	0.17	0.15

metal were calculated from the data used previously (46). The "measured P_B" was calculated from rates of loss of boron which were obtained by subtracting the loss of molybdenum from the shield gain. The small losses of boron made it impossible to obtain analytical data for these runs. The K_p used for each temperature was read from the curve of Figure III which was drawn to have a slope corresponding to a heat of vaporization of 478.3 kcal.

The data show that the entire weight loss can be attributed to loss of molybdenum, nevertheless molybdenum appears, so that boron is lost at a rate greater than 1/2 that of the metal. It follows therefore that according to Langmuir's equation, P_B is greater than 0.168 P^o_{Mo}. On these grounds, P_B may be fixed in the range $0.168\ P^o_{Mo} < P_B < P^o_{Mo}$ in the two phase region. The calculated P_B/P^o_{Mo} may be considered to be in agreement with observations in light of the necessarily limited weight losses.

5. Stability of MoB

Vapor pressure measurements could be used to determine the stability of MoB in either of two ways. In the first case, the equilibrium constant for the process

$$MoB(s) = Mo(g) + B(g)$$

could be measured in a manner similar to that used for Mo_2B. MoB has a range of homogeneity, however, so that an additional determination other than rates of loss and composition of vapor would be needed, namely, the composition of the surface from which vaporization

had occurred. An alternative method would be to heat $MoB_{0.96}$ in the presence of Mo_2B or Mo_3B_2 in an effusion or rate-of-evaporation experiment. In such a case, the composition of the two phases would be fixed according to the phase law and the system would be completely defined. The predominant process would consist in the preferential loss and resultant conversion of the higher boride to the lower one, but nevertheless the two processes

$$MoB_{0.96}(s) = Mo(g) + 0.96B(g)$$

$$Mo_2B(s) = 2Mo(g) + B(g)$$

would occur to some extent so that the corresponding equilibrium constants would have to be satisfied. Determination of these equilibrium constants would permit making calculations of the stabilities of both solid phases. One might also perform the experiment with MoB and MoB_2. The difficulty that was anticipated in this type of experiment was that the results would suffer in accuracy as a result of the low partial pressure of Mo that might be expected and the consequent small weight loss of the metal. Because of these factors, a second possibility was selected and will be described below.

The method used consisted in measuring the equilibrium pressure for the reaction

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g),$$

The free energy change for the above process could be combined with other data to obtain the stability of $MoB_{0.96}$ as shown later. It should be noted that the temperature of the experiment must be kept

to a value at which Mo_3B_2 cannot exist. On the basis of the work of Steinitz and his colleagues (9) and of the work performed in this laboratory (11), it was estimated that experimental temperatures could not be greater than approximately 2200° K.

The sample used for the experimental work to be described below consisted of sample number 86 after the outer layer of Mo_2B had been ground off on a grinding wheel. This sample had been used in studies of the reaction

$$Mo_2B(s) = 2Mo(g) + B(g).$$

The reason for selecting such a sample was to take advantage of the extensive heating which should have produced purification and sintering.

The apparatus and heating procedure used for the experiments were identical to those used in the previous experiments. The general procedure consisted in grinding the sample to assure exposure of a Mo_2B - MoB surface, degassing for about five minutes at 1700 to 1800° C. heating for the purpose of taking data, and then examining the surface after the data run to make sure of the presence of the two solid phases. The sample and parts of the assembly were weighed after the degassing run with minimum exposure to the atmosphere. Weight losses of the sample were about 2 to 3 mgms during degassing and approximately 1 mgm during heatings for data-taking purposes. The data are summarized in Table XIV. Sublimates were not analyzed for boron.

Table XIV

Summary of Data for the Process

$MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g)$

Run	86 m	86 o	86 q	86 s
(1) net loss, mgms	1.0	1.0	0.9	1.4
(2) shield gain, mgms	0.6	0.8	0.9	1.1
(3) area, cm^2	8.1	8.1	8.0	7.8
(4) time, sec.	1080	1200	900	3300
(5) Temp. ^oK	2103	2098	2161	2084
(6) P_B, atmospheres	$2.1x10^{-8}$	$2.6x10^{-8}$	$3.9x10^{-8}$	$1.3x10^{-8}$
(7) P^o_B, atmospheres	$1.3x10^{-7}$	$1.2x10^{-7}$	$3.0x10^{-7}$	$9.2x10^{-8}$
(8) $\Delta F^o/T = -(0.92)(4.58) \log P_B$ cal/deg.	32.4	31.9	31.2	33.2
P_B/P^o_B	0.16	0.22	0.13	0.14

Runs 86 l, n,p and r were degassing runs which followed grinding of the cylinder. Runs 86 m, o, q and s were followed by x-ray examination which showed the presence of both Mo_2B and MoB at the surface in each case. The data on net loss, shield gain, area, time, and temperature given in Table XIV were determined in the same manner as that used for the corresponding data presented in Table VIII relative to the experiments on Mo_2B. The pressure of boron, P_B, was computed on the basis of shield gains on the assumption that loss of molybdenum was negligible. That such an assumption was justified could be shown by computing the weight of molybdenum that would be lost from the pure metal using the data of Johnston, Edwards and Blackburn. The estimated loss from pure metal would be approximately 0.2 mgms, and the loss molybdenum from the Mo_2B - MoB surface could be expected to be less.

The data obtained in the experiments above will be used with free energy functions to compute the value of ΔH°_{298} for the reaction

$$0.92B(s) + Mo_2B(s) = 2MoB_{0.96}.$$

If the assumption is made that $-(F^\circ - H^\circ_{298})/T$, that is, the free energy function, of the compounds are equal numerically to the sum of the free energy functions of the elements as was done for the preceeding calculations, then it can be shown that for the reaction

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g)$$

the change in free energy functions is numerically equal to that

for the process

$$0.92B(s) = 0.92B(g).$$

The quantity H°_{298}/T for the process

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g)$$

may be found by use of the equation

$$H^{\circ}_{298}/T = -(F^{\circ} - H^{\circ}_{298})/T \quad F^{\circ}/T$$

where the free energy function can be computed as indicated above and $\Delta F^{\circ}/T$ can be computed as indicated in the next to the last row of Table XIV. The computations outlined above were made and are summarized in the Table below.

Table XV

Summary of Thermodynamic Data for $MoB_{0.96}$

Run	86 m	86 o	86 q	86 s
Temp. °K	2103	2098	2161	2084
$\Delta F^{\circ}/T$ = $-0.92(4.58)\text{Log } P_B$	32.4	31.9	31.2	33.2
$-(\Delta F^{\circ} - \Delta H^{\circ}_{298})/T$	32.4	32.4	32.4	32.4
$\Delta H^{\circ}_{298}/T$	64.6	64.3	63.6	65.6
ΔH°_{298}, kcal	136.3	134.9	137.4	136.7

Avg ΔH°_{298} = 136.3 kcal

P.E. = $0.6745\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}}$ = 0.3 kcal.

The data summarized in the preceeding table may be combined with heats of vaporization of boron given by Searcy and the heat of formation of Mo_2B to obtain a heat of formation for $MoB_{0.96}$. The operations are illustrated below.

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g) \qquad \Delta H^\circ_{298} = 136.3 \text{ kcal}$$

$$0.92B(g) = 0.92B(s) \qquad \Delta H^\circ_{298} = -0.92(140.9) = -129.5 \text{ kcal.}$$

Addition of the equations above and reversing the result gives

$$Mo_2B(s) + 0.92B(s) = 2MoB_{0.96} \qquad \Delta H^\circ_{298} = -6.8 \text{ kcal.}$$

Work on the stability of $Mo_2B(s)$ has shown that the heat of formation ΔH°_{298}, from the elements is -25.5 kcal per gram mol, from which by combination with the preceeding results,

$$2Mo(s) + 1.92B(s) = 2MoB_{0.96} \qquad \Delta H^\circ_{298} = -32.3 \text{ kcal.}$$

or, for one gram mol, the heat of formation at 298° K is -16.2 kcal.

It is also possible to show by combining heats of formation that Mo_2B does not disproportionate. Thus, writing according to the convention of Lewis and Randall,

$$0.96Mo_2B(s) = 0.92Mo(s) + MoB_{0.96}$$

$$(0.96)x(-25.5) \qquad 0+0 \qquad -16.2 \qquad \Delta H^\circ_{298} = 8.3$$

From the reaction above, the process is seen to be endothermic, so that Mo_2B is thermodynamically stable with respect to disproportionation into Mo and $MoB_{0.96}$, since $(\Delta F^\circ - \Delta H_{298})/T$ is assumed to be zero.

The ratios, P_B/P_B^o in Table XIV are seen to vary from 0.13 to 0.22 with no trend with temperature being evident. The uncertainty in temperature measurement is believed to be partially responsible for this variation. The errors due to the small weight losses were a consequence of the necessity for limiting heatings to a time during which MoB could remain on the sample surface. No ambiguity in these results accrue because of the existence of the high temperature phase Mo_3B_2, since care was exercised to keep experimental temperatures below that at which the boride is thought to disproportionate.

The available data may be used to calculate the partial pressures of boron and molybdenum in equilibrium with Mo_2B and $MoB_{0.96}$. Such calculations will be shown below for a temperature of 2200°K and will utilize free energy function data tabulated elsewhere in this report. Thus, from Table X the free energy function, $-(\Delta F^o - \Delta H^o_{298})/T$, for the reaction

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g)$$

is estimated to be 32.4 units. According to the data summarized in Table XV, ΔH^o_{298} for the process is 136,300 calories, so that

$$-\Delta F^o/T = -(\Delta F^o - \Delta H^o_{298})/T - 136,600/T$$

$$= -29.8 \text{ e.u.}$$

$$4.58(0.92) \text{ Log } P_B = -29.8$$

$$\text{Log } P_B = -7.08$$

$$P_B = 1.00 \times 10^{-7}$$

From earlier calculations, it was found that for the vaporization of Mo_2B, the corresponding equilibrium constant, $(P_{Mo})^2(P_B)$ is 2.4×10^{-25} at 2200°K. Solving for P_{Mo} when $P_B = 1.00 \times 10^{-7}$ atmospheres give $P_{Mo} = 1.6 \times 10^{-9}$, approximately 1/60 P_B, thus verifying the previous assumption that in the Mo_2B - $MoB_{0.95}$ region the loss of molybdenum is negligible in comparison with the loss of boron.

6.Stability of Mo_3B_2

The stability of Mo_3B_2 could not be determined directly however conclusions regarding that compound may be reached by using the heats of formation of Mo_2B and $MoB_{0.96}$ together with the fact that all three compounds can exist simultaneously at about 2200° K.

In the discussion that follows, it will be assumed that the free energy function for the compound is equal to the sum of the free energy functions of the elements. This is the same approximation made in the case of Mo_2B and $MoB_{0.96}$. It will also be assumed that Mo_3B_2 has a definite composition, that is, that there is no extensive homogeneity range. Steinitz, Binder and Moskowitz have found that Mo_3B_2 is isomorphous with Cr_3B_2, a fact which indicates similar crystal structure and binding. Although the above authors were not able to study the high temperature phase in detail, the similarity to the chromium boride and the fact that Kiessling indicates a negligible range of homogeneity for Cr_3B_2(37) would suggest that the assumption made above with regard to Mo_3B_2 is

justified.

If the reaction between Mo_3B_2, Mo_2B and $MoB_{0.96}$ is written as shown and it is recalled that $-(\Delta F^\circ - \Delta H^\circ_{298})/T$ for the reaction is zero because of the approximation made, then

$$0.92Mo_3B_2(s) = 0.88Mo_2B(s) + MoB_{0.96}$$

and

$$\Delta H^\circ_{298}/T = -(\Delta F^\circ - \Delta H^\circ_{298})/T - \Delta F^\circ/T = 0$$

where $\Delta F^\circ/T = 0$ as a result of the equilibrium that can exist at some temperature.

The heats of formation of the compounds on the right hand side of the above reaction may be combined in the usual manner to give for the reaction

$$3Mo(s) + 2B(s) = Mo_3B_2 \qquad \Delta H^\circ_{298} = -42.1 \text{ kcal.}$$

7. Stability of MoB_2

Information regarding the stability of MoB_2 was obtained by measuring the equilibrium pressure for the process

$$MoB_{2.14}(s) = MoB_{1.06}(s) + 1.08B(g)$$

In this discussion, the formulae MoB and MoB_2 will be used for convenience in referring to the compounds of composition shown above. Data for the reaction are limited to those obtained during one run during which a group of five small samples, weighing from 0.25 to 0.38 gm were heated simultaneously in a 1.25 inch diameter

molybdenum crucible in a "getter" experiment. The details of the experiment differed considerably from those of the preceeding work and will be described below.

Preparations and experiments were carried out in apparatus No. 2. A 1.25 inch diameter Fansteel molybdenum crucible was used as both a container and heating element in a heating arrangement described elsewhere.

Five small samples, weighting from 0.25 to 0.38 gm were prepared from molybdenum batch No. 1 and boron batch No. 1 by packing the various powder mixtures into quartz vials and heating for one hour at 1350° C. and then for a half hour at 1600° C. A portion of each sample was examined by x-ray diffraction to make sure reaction was complete. Assay by chemical means could not be made because of analytical difficulties at the time the work was underway. The second portion of each sample in the form of a cylindrical plug about 1/2 cm in diameter was outgassed for one hour at about 1825° C. during which weight losses of 1.5 to 4.5 mgms were observed. The data for the second heating are tabulated in Table XVI.

The second heating to which the samples were subjected was carried out in the same manner as for the outgassing run. Each sample was suspended inside an individual cylindrical molybdenum shield made from 0.002 inch sheet. The samples were suspended by means of a 0.010 inch molybdenum wire passing through a hole down

the center of each sample. No sample could "see" any other. After the outgassing run and after the data run, parts of the heater and contents were examined visually for evidence of attack by vapor. It was found that parts of the shields cast sharp shadows and no evidence of reflection of vapor could be detected. It was assumed therefore, that the getter experiments gave results comparable to those that would have been obtained in a more conventional Langmuir technique in which the accommodation coefficient was unity.

The data for the run described above are summarized in Table XVI. The ratio B/Mo refers to the atomic ratio of the boron and molybdenum powder prior to heating to cause reaction. No analytical data were obtained for these samples. Initial weights and weight losses need no comment. The areas were computed from measurements of diameter and lengths of the individual samples but because of irregularities in the samples, are reported to only two significant figures. The time and temperature were determined from a time-temperature plot as for preceeding work, the temperature being corrected for pyrometer and window errors as was done in the work described before. The apparent P_B was calculated on the basis that the external area was the true or effective area of vaporization. P_B^o was calculated on the basis of the same data as was used for Mo_2B and $MoB_{0.96}$.

Table XVI

Summary of Data for the Reaction

$MoB_{2.14}(s) = MoB_{1.06}(s) + 1.08\ B(g)$

Sample	1	2	3	4	5
B/Mo, originally (by synthesis)	1.0	1.3	1.5	1.8	2.2
Initial weight gm	0.3178	0.3798	0.3084	0.2504	0.2101
Weight loss, mgms	0.1	0.2	0.4	1.0	2.0
areas, cm^2	1.5	1.7	1.6	1.5	1.4
Time, sec.	5000	5000	5000	5000	5000
Temp. °K	2159	2159	2159	2159	2159
P_B apparent	-	-	-	0.5×10^{-9}	0.9×10^{-7}
P_B^o	2.9×10^{-7}	2.9×10^{-7}	2.9×10^{-7}	2.9×10^{-7}	2.9×10^{-7}

After The data run, the samples were broken open and examined visually. It was found that samples 1, 2, and 3 were uniformly grey in color. Samples 4 and 5 had a blue-black inner core and a grey outer layer. The core of sample 5 was the larger. X-ray examination of the samples showed that the inner core contained MoB_2 and that the outer layer was MoB. Spectroscopic examination of the samples also were made and showed that silicon to the extent of 0.1 to 1.0% was the principal impurity, with traces of iron being found. The silicon was probably derived from the quartz vials used in the preparations.

It appears that, from the small weight losses relative to the total weight of samples and to the extensive conversion of MoB_2 into the lower boride, boron is the principle gaseous species evolved and that no gaseous boride could be of importance. It appears also that the preferential loss of boron leaves a layer of a lower boride and that either the effective area of vaporization is smaller than the superficial area, or that the outer layer interferes with vaporization, or that a combination of both of the above effects occurs. The data described above indicate that the apparent value of P_B is low. In the absence of other information, the equilibrium pressure for this reaction will be estimated to be 1/2 the vapor pressure of boron in the range of temperature around 2200° K and calculations will be made on that basis.

It is possible to estimate the partial pressure of molybdenum in equilibrium with MoB and MoB_2 from available data by applying the Gibbs - Duhem equation, (50)

$$N_1 \; d\ln \; a_1 = -N_2 \; d\ln \; a_2$$

through the MoB range and by assuming that the activity of boron in MoB changes in the simple way given by

$$a_B = K(N_B/N_{Mo}) + C$$

The constants of the above equation can be evaluated from the compositions at the ends of the MoB solid solution, $N_B/N_{Mo} = 0.96$ and 1.06, and the partial pressures of boron, $0.18P_B^\circ$ and $0.50P_B^\circ$ on opposite sides of the region. Thus,

$$a_B = 3.2 \; N_B/N_{Mo} - 2.89.$$

By rearranging the Gibbs - Duhem equation, making the appropriate substitutions and performing the indicated integration

$$\int_{a_B = 0.18}^{a_B = 0.50} d\text{Log } a_{Mo} = -\int_{a_B = 0.18}^{a_B = 0.50} N_B/N_{Mo}) \; d\text{Log } (3.2N_B/N_{Mo} - 2.89)$$

it is found that the ratio of the activity of molybdenum in $MoB_{1.06}$ to its activity in $MoB_{0.96}$ is 0.36. Thus, the partial pressure of molybdenum in equilibrium with MoB and MoB_2 is given by

$$P_{Mo} = 1.2 \times 10^{-9} \times 0.36 = 4.3 \times 10^{-10} \text{ atm.}$$

where the number 1.2×10^{-9} is the pressure of molybdenum in atmospheres in equilibrium with Mo_2B and $MoB_{0.96}$ as calculated

from previously determined heat and free energy function data.

The equilibrium partial pressure of molybdenum and of boron may be used in the usual way to show that for the reaction

$$MoB_{1.06}(s) = Mo(g) + 1.06B(g) \quad \Delta H^{\circ}_{298} = 322.3 \text{ kcal}$$

Combination of the above heat of vaporization with that for one mol of molybdenum and 1.06 mols of boron gives for the heat of formation of $MoB_{1.06}$

$$Mo(s) + 1.06B(s) = MoB_{1.06}(s) \qquad H^{\circ}_{298} = -16.9 \text{ kcal.}$$

Treatment of equilibrium pressure data as illustrated previously shows that for the reaction

$$MoB_{2.14}(s) = MoB_{1.06}(s) + 1.08B(g) \quad \Delta H^{\circ}_{298} = 155.1 \text{ kcal.}$$

and that for

$$Mo(s) + 2.14B(s) = MoB_{2.14}(s) \qquad \Delta H^{\circ}_{298} = -19.8 \text{ kcal.}$$

that is, all solid phases are formed from the elements by an exothermic reaction.

The partial pressure of molybdenum in the MoB_2 - B region and the heat of formation of $MoB_{2.33}$ may be found in the same manner as for $MoB_{1.06}$. Thus it is found that the partial pressure molybdenum in equilibrium with $MoB_{2.33}$ and B is

$$P_{Mo} = 0.21 \times 4.3 \times 10^{-10} = 0.90 \times 10^{-10} \text{ atm.}$$

and that for the reaction

$$MoB_{2.33}(s) = Mo(g) + 2.33B(g) \qquad \Delta H^{\circ}_{298} = 504.2 \text{ kcal.}$$

and that for

$$Mo(s) + 2.33B(s) = MoB_{2.33}(s) \qquad \Delta H^{\circ}_{298} = -19.9 \text{ kcal.}$$

The partial pressures of boron and molybdenum in different regions of the phase diagram at 2200° K are shown in Figure IV.

H. Summary of Work on the Molybdenum Borides

During the course of experimental work on the molybdenum borides some phase studies were made which confirm the existence of a high temperature phase, Mo_3B_2 reported by Steinitz, Binder and Moskowitz but differ from results of these authors in that melting temperatures found in this laboratory were higher by 100 to 175 degrees. Melting points in the range of composition including Mo_2B and MoB were found to lie in the range of temperature from 2100 to 2375° C.

Vaporization processes were studied by means of weight loss determinations, analyses of sublimates, time and temperature data, and x-ray diffraction examinations as principal tools. As a result of four kinds of vaporization experiments, stabilities and equilibrium pressures in the molybdenum system could be found. The experiments and results are summarized briefly below. (1) Experiments with cylinders having a MoB core and Mo_2B surface. Data on these experiments, when interpreted in terms of B(g) coming from MoB to decrease P_{Mo} at the surface permitted making measurements of K_p's and yielded for the processes

$$Mo_2B(s) = 2Mo(g) + B(g) \qquad \Delta H_{298} = 478.3 \text{ kcal.}$$

$$2Mo(s) + B(s) = Mo_2B(s) \qquad \Delta H_{298} = -25.5 \text{ kcal.}$$

Data include weight loss, weight gain of shields, and sublimate analyses all estimated accurate to 10 - 20 percent.

If a stable gaseous boride were being formed in the vaporization the heat of vaporization would have been higher than that taken which

would lead to a more negative heat of formation. Since the present value is consistent with that of Brewer and Haraldsen, the possibility of stable gaseous borides is considered negligible. (2) Experiments with cylinders of Mo_2B show that entire weight losses can be attributed to molybdenum because of the vapor pressure of the free metal, however, solid metal appears thus requiring that boron be lost more rapidly than 1/2 the rate of loss of molybdenum. On the basis of the Langmuir expression, it is possible to limit the value of P_B in equilibrium with Mo and Mo_2B as follows:

$$0.168P^{\circ}_{Mo} < P_B < P^{\circ}_{Mo}$$

Calculations based on the equilibrium constant for the vaporization of Mo_2B indicate that $P_B \sim 1/6\ P^{\circ}_{Mo}$, so that results are consistent. The existence of an important gaseous boride is excluded by these results because if such existed the observed pressure would be greater than that to be expected on the basis of metal alone vaporizing.

Data taken included weight losses and weight gains accurate to about 20 percent. Sublimate analyses could not be made but would have been useful. (3) Experiments with MoB cylinders on the surface of which Mo_2B formed rapidly so that runs had to be kept short in order to keep $MoB_{0.96}$ present, showed P_B to be higher than for the Mo_2B experiments and that for

$$2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g) \qquad \Delta H^{\circ}_{298} = 136.3 \text{ kcal.}$$

whence

$$Mo_2B(s) + 0.92B(s) = 2MoB_{0.96}(s) \qquad \Delta H^{\circ}_{298} = -6.9 \text{ kcal.}$$

and

$$2Mo(s) + 1.92B(s) = 2MoB_{0.96}(s) \qquad \Delta H^{\circ}_{298} = -32.3 \text{ kcal}$$
$$= -16.2 \text{ per mol.}$$

They showed further that

$$0.96\ Mo_2B(s) = 0.92Mo + MoB_{0.96}(s) \qquad \Delta H^{\circ}_{298} = 8.3 \text{ kcal}$$

and therefore Mo_2B does not disproportionate.

Combination of data on P_B and K_p for vaporization of Mo_2B shows that $P_{Mo} = 1/60\ P_B$ in the two phase region including Mo_2B and $MoB_{0.96}$ so that the weight loss of Mo was negligible.

Since Mo_3B_2 just barely disproportionates into Mo_2B and $MoB_{0.96}$ that is, for the reaction

$$0.92\ Mo_3B_2(s) = 0.96\ Mo_2B(s) + MoB_{0.96} \qquad \Delta H^{\circ}_{298} = 0$$

it is possible to use the heats of formation of Mo_2B and $MoB_{0.96}$ to obtain for the reaction

$$3Mo(s) + 2B(s) = Mo_3B_2(s) \qquad \Delta H^{\circ}_{298} = -48.1 \text{ kcal}$$

Data on which the results obtained above were based included weight losses and gains of approximately one mgm. No analytical data could be taken. (4) Experiments with $MoB_{1.06}$ - $MoB_{2.14}$ cylinders were carried out using the getter technique and gave data that permitted making an estimate of P_B. Accurate data could not be taken because of the rapid loss of boron which left an outer layer of MoB. On the basis of estimated P_B of one-half the vapor pressure and the assumed applicability of a modification of Raoult's law to MoB, the P_{Mo} in

equilibrium with $MoB_{1.06}$ and $MoB_{2.14}$ was found to be 4.3×10^{-10} atm. and the heat for the reaction

$$Mo(s) + 1.06B(s) = MoB_{1.06}(s)$$ was found to be -16.9 kcal.

From the reaction

$$MoB_{2.14}(s) = MoB_{1.06}(s) + 1.08B(g)$$

the heat for

$$Mo(s) + 2.14B(s) = MoB_{2.14}(s)$$

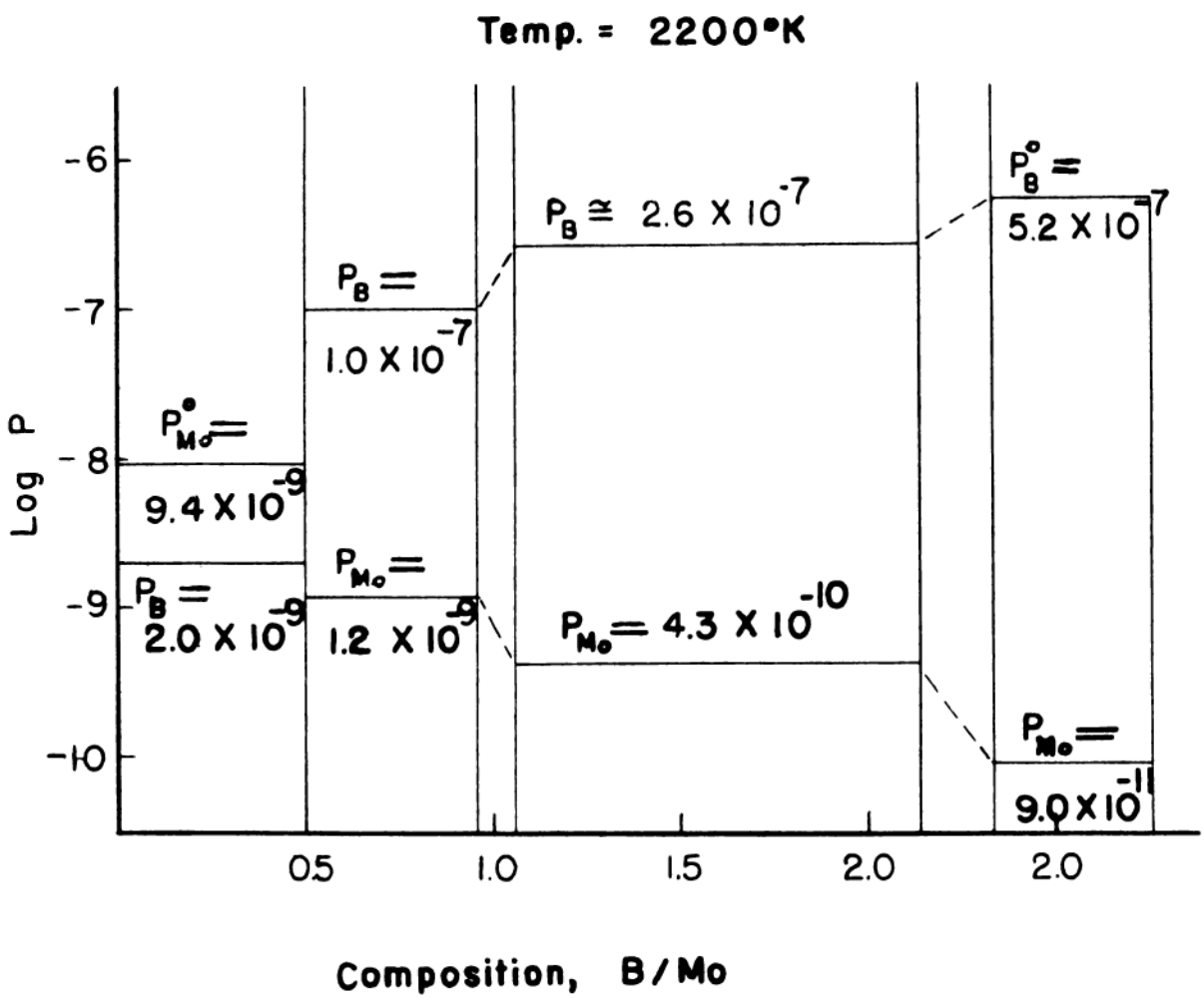
was determined as -19.8 kcal.

Treatment of MoB_2 in a manner similar to that for MoB gives for

$$Mo(s) + 2.33B(s) = MoB_{2.33}(s) \quad \Delta H^{\circ}_{298} = -19.9 \text{ kcal}$$

and a pressure of molybdenum in equilibrium with $MoB_{2.33}$ and B as being 0.9×10^{-10} atm.

FIGURE 4
PRESSURE - COMPOSITION
DIAGRAM



I. Suggestions for Future Work

As a result of the experience gained during this investigation a number of suggestions concerning equipment and techniques have been made in another report (28) and will not be discussed here.

The equilibrium pressure data for the reaction

$$MoB_{2.14}(s) = MoB_{1.06}(s) + 1.08B(g)$$

obtained in this work were quite meager and it is suggested that additional experiments be conducted to extend the number and accuracy of such data. For such determinations, the Knudsen method appears to be most satisfactory and for that work it is suggested that graphite crucibles would be satisfactory (40, 44). Should these experiments be attempted, the writer has two suggestions based on his experience. First, it would be highly desirable to obtain boron of greater purity than the commercial product now on the market. The material used in this investigation had iron as one principal impurity together with minor amounts of other volatile materials such as magnesium and calcium. Loss of these impurities during effusion experiments would subject effusion data to possible excessive errors since total loss of material during such experiments is usually small, that is, of the order of mgms.

The second suggestion concerns the desirability of mastering a suitable spectrophotometric method of analysis of boron. If collector plate techniques are to be used, a micro analytical method of analysis of boron, such as that utilizing quinalizarin as a color-forming

reagent in a spectrophotometric procedure, would be essential. The writer was not successful in obtaining any color change with this reagent and therefore suggests that this analytical problem be solved first.

Johnston, Hersh and Kerr have obtained the low temperature thermal data on crystalline and amorphous boron (51). Their heat capacity at 298° K is 2.650 calories/mol/degree as compared to 2.066 calories/mol/degree for graphite. It appears therefore that boron behaves in a manner similar to that of graphite so that Debye functions could be used to extend the low temperature data to higher temperatures.

Brewer and his students have studied relative stabilities of the borides (16a,b) and suggest the possible value of TaB_2 and ZrB_2 as crucible materials for use at high temperatures. According to Kiessling, (4), the Ta - B system is rather complicated, however, zirconium forms only one boride, and the metal dissolves boron to the extent of about one percent. An estimate of the equilibrium constant for the process

$$ZrB_2(s) = Zr(g) + 2B(g)$$

at 2400° K based on an assumed stability of 84 kcalories indicates that there is a high probability that the compound may vaporize as a constant subliming phase. Vapor pressures at the temperature chosen may be expected to be of the order of 7×10^{-8} to 10^{-7} atmospheres. The techniques used in this investigation should therefore

prove feasible for the study of ZrB_2.

Heats of formation of borides may be found indirectly by determinations of heats of combustion. Such heats may be used in combination with heats of combustion of the elements to find the desired heat of formation. It is possible that such heat data may not be readily obtained because of difficulty in obtaining definite reaction products, however, an alternate method would be to study the reaction of various compounds such as MoB with mixtures of H_2 and H_2O vapor. The activity of oxygen could be varied by varying the relative amounts of H_2 and H_2O and by varying the total pressure. In the case of MoB, the reaction to be expected would be

$$2MoB + 3/2H_2O \rightleftharpoons Mo_2B + 1/2B_2O_3 + 3/2H_2.$$

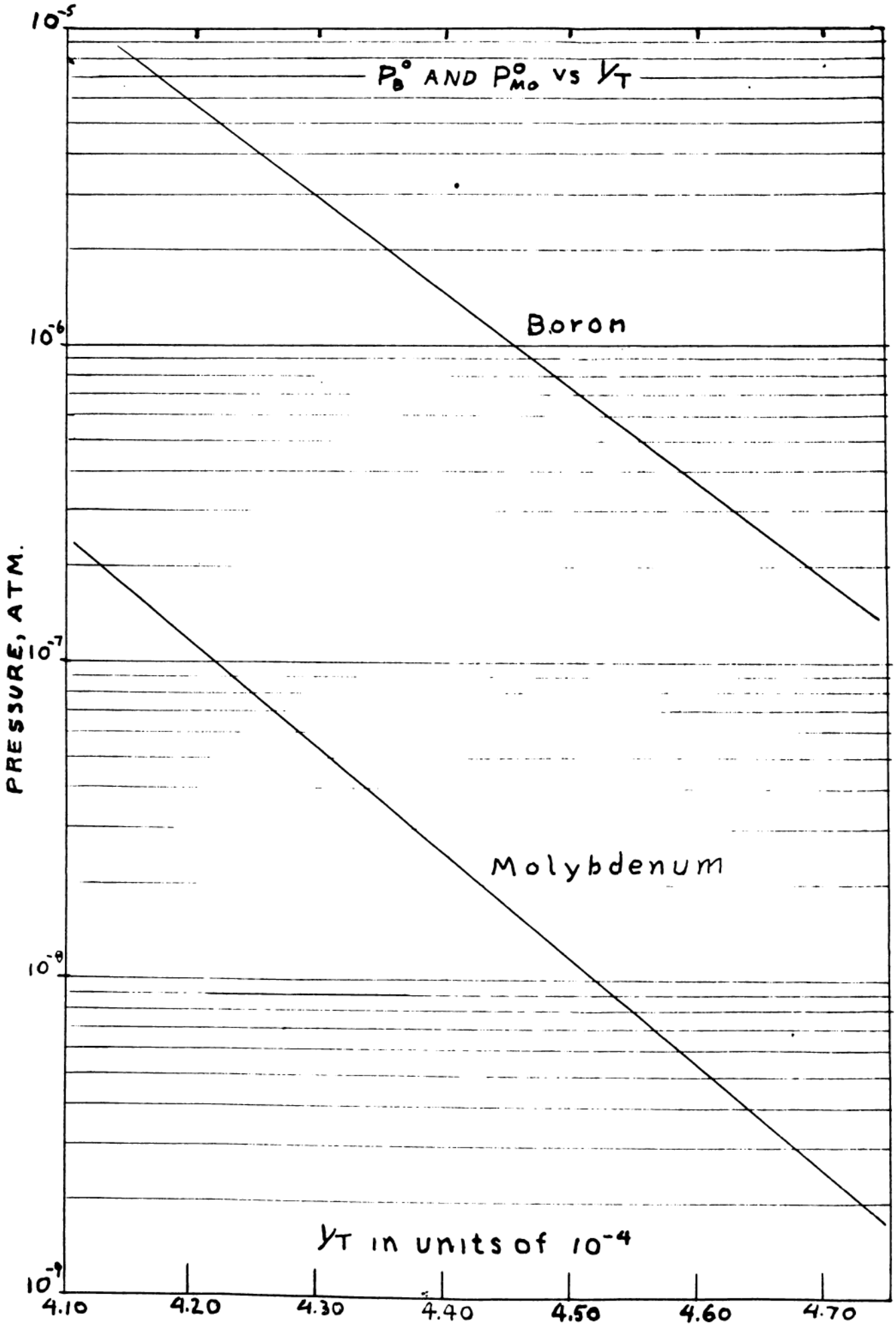
Equilibrium constants determined for the reaction above in combination with thermodynamic data for boric oxide and water should permit making a calculation for the reaction

$$Mo_2B + B = 2MoB.$$

It is suggested that the experiments be carried out at temperatures greater than about 400° C. in order that reaction rates be great enough to be practical. Maximum temperatures could be about 1000° C. at which accurate temperature measurement and equipment design should not pose excessive difficulty.

The hardness of the borides of molybdenum and of other transition metals, which is of the order of 9 on Moh's hardness scale (52),

suggests that they may find practical application as machine tool material. It is probable that their practical employment would depend on their use with some binder element, as in the case of tungsten carbide and cobalt (1). This possibility therefore suggests that phase diagram studies involving a transition metal, boron and possible binders such as copper, iron, nickel or cobalt may prove valuable.


P_B° AND P_{Mo}° VS $1/T$
Boron
Molybdenum
PRESSURE, ATM.
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
$1/T$ in units of 10^{-4}
4.10
4.20
4.30
4.40
4.50
4.60
4.70

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