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AECU-2894

AT-11-1-83
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[Contribution from the Department of Chemistry,
University of Kansas, Lawrence]

no 43893

The Thermodynamic Properties and Equilibrium Pressures
in the Molybdenum-Boron System¹.

by

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(1) Abstracted in part from the Ph.D. thesis of Bernard D. Pollock, September, 1953. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Ill., September 9, 1953.

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Abstract

In the molybdenum-boron system there are four compounds, or homogeneity ranges, and six crystal structures, Mo_2B , Mo_3B_2 , $\alpha\text{-MoB}_{1+x}$, $\beta\text{-MoB}_{1+x}$, $\alpha\text{-MoB}_{2.25\pm y}$, and $\beta\text{-MoB}_{2.25\pm y}$. . . From a study of the vapor pressures of these compounds and their mixtures by the Langmuir technique, their stabilities, heats of formation, and the partial pressures of the elements in equilibrium with the solid phases have been determined. Table V contains values of ΔH_{298}° , the heats of formation of the compounds, calculated from the vapor pressures on the assumption that ΔS and ΔC_p for solid reactions are both zero. These values, with the heats of sublimation of Mo and B of $\Delta H_{298}^{\circ} = 155.94^{10}$ and 140.9^{12} , the published free energy functions of $\text{Mo}^{10,11}$ and B^9 , and the above assumption, may be used to calculate the high temperature behavior of this system. Fig. 1 shows the partial pressures of the monatomic elements at 2200°K in equilibrium with one or two solid phases having the overall composition indicated. It is shown that solid compositions having more B than Mo_2B rapidly lose B preferentially. Furthermore, in Langmuir or Knudsen experiments, Mo_2B loses B more rapidly than one-half the rate of Mo loss, so that in such experiments Mo(s) appears and there is no constant subliming composition. In a closed system, however, Mo_2B would evaporate to give a gas having the same composition. It is demonstrated that there are no gaseous molecules of any importance in the Mo-B system at high temperature.

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Because of their high melting points, low vapor pressures, metallic properties, and good conductivity, the transition metal borides promise to become increasingly important in high temperature systems. Their inertness to most reagents and the difficulty of obtaining products of definite composition make determinations of their thermodynamic properties by the usual calorimetric techniques impossible. Under such circumstances, measurements of their vapor pressures and studies of their vaporization processes at high temperature can yield important thermodynamic data.

This paper presents the results of vaporization studies on a typical transition metal-boron system, that of the molybdenum borides, and gives the heats of formation of several compounds and the partial pressures of molybdenum and boron in equilibrium with the various solid phases.

The phase diagram of the molybdenum-boron system has recently been studied^{2,3,4,5} and shows four compounds and six crystal

(2) R. Steinitz, J. Metals 4, 148 (1952).

(3) R. Steinitz, I. Binder, and D. Moskowitz, J. Metals 4, 983, (1952); P. Rautala, J. Metals 5, 747 (1953).

(4) Paul W. Gilles and Bernard D. Pollock, J. Metals 5, 1537 (1953).

(5) Paul Schwarzkopf and Richard Kieffer, Refractory Hard Metals, MacMillan, New York, 1953.

structures. At room temperature Mo_2B (CuAl_2 tetragonal structure), $\alpha\text{-MoB}_{0.96-1.06}$ (tetragonal), and $\alpha\text{-MoB}_{2.14-2.33}$ (rhombohedral) are stable, while Mo_3B_2 (isomorphous with tetragonal Cr_3B_2), $\beta\text{-MoB}_{1.00-1.06}$ (isomorphous with orthorhombic CrB), and $\beta\text{-MoB}_{2.14-2.33}$ (AlB_2 hexagonal structure) are stable only at high temperature. There is little solubility of boron in the metal. The homogeneity ranges

of Mo_2B and Mo_3B_2 apparently are small. Around MoB there is wide solid solubility but the β phase exists only if boron is present in excess of the 1-1 ratio. The low and high temperature forms of $\text{MoB}_{2.14-2.33}$ lie between the compositions corresponding to MoB_2 and Mo_2B_5 . Samples having either of these two stoichiometric compositions have two phases.

The Langmuir evaporation or Knudsen effusion method was used for experiments with four kinds of samples: (1) ones with a core of $\text{MoB}_{0.96}$ or Mo_3B_2 and a Mo_2B surface, (2) ones of pure Mo_2B , (3) ones with a core of $\text{MoB}_{0.96}$ and a surface of both Mo_2B and $\text{MoB}_{0.96}$, and (4) ones with a mixture of $\text{MoB}_{1.06}$ and $\text{MoB}_{2.14}$:

EXPERIMENTAL

Materials.-- The samples were prepared from commercially obtained molybdenum and boron. The 400 mesh Mo powder was purchased as 99.9% material with oxygen as the principle impurity and nitrogen, C, Fe, and Ni in trace amounts. It was found to oxidize slowly on exposure to the atmosphere. One and one-half years after purchase, an assay showed 99.4% following a vacuum outgassing for 5 min. at 1000°C . which caused a wt. loss of 0.3%.

The 325 mesh B powder was purchased as 99.0% or better material with Fe and C as the principal impurities; but, as with Mo, oxidation resulted on exposure to the atmosphere. Assays on samples that had been vacuum outgassed for about 10 min. at about 1700°C in a Mo crucible, during which a wt. loss of 3 to 4% occurred, showed 98% or better except for one sample that showed 95.5% following recovery after an accident.

Samples.-- The cylinders used for most of the vaporization experiments were about 2 cm. x 2 cm. and were prepared from the above materials by a four-step process: (1) pre-treatment of the elements to accomplish purification, (2) reaction of the elements to form the compounds, (3) pre-sintering of the cylindrical sample,

and (4) final sintering and purification.

Pre-treatment of the elements consisted of heating, according to the schedule used for the above assays, cylinders that had been pressed in a steel die.

Powdered elements, obtained by grinding the pre-treated cylinders, were mixed for the second step in appropriate proportions with an excess of usually 3% boron to compensate for impurities, and the resulting mixtures were compacted by a pressure of about 6000 psi without binder or lubricant.

It was found that complete reaction was accomplished if such compacts were heated in molybdenum crucibles in vacuum, slowly at first to eliminate occluded gases, then to 1000° to 1200°C for several minutes to allow the reaction to occur, and then to 1400 to 1800°C for 10 to 15 min. to effect some purification by vaporization of the more volatile substances. The exothermic preparation reactions caused 25 to 35 gm. batches to show temperature rises of 50 to 300°C. At this stage of the process considerable purification had occurred; e.g., a boride sample prepared from the worst B assayed 99.5%.

The occasional necessary readjustment of composition was accomplished by similar procedures.

In the third stage of the process, powders obtained by grinding of the cylinders from the second stage, were pressed without binder or lubricant into cylindrical shapes by pressures of 12,000 to 14,000 psi. The cylinders were then pre-sintered to give the compact enough strength to allow the drilling of black body holes. The temperatures used were about 1500°C for Mo₂B samples and 1900°C for MoB samples.

After the presintered cylinders had been drilled, they were heated in vacuum in the last step to about 2100° to 2250°C. by means of their own conductivity for final sintering and purification. During this heating the vol. decreased by 30 to 35%. Wt. loss data indicated that for one sample, presumably the worst, the purity was 99.8 to 99.9%. Sometimes before use or between experiments the cylinders were ground on an electric grinding wheel until true.

Analyses.--Assays for Mo and B, either free or combined, were performed by the lead molybdate method and the Blumenthal⁶ method

(6) H. Blumenthal, Anal. Chem. 23, 992 (1947).

respectively; and although considerable difficulty was encountered, they were reliable to about 0.25% and 1% relative, respectively.

The determination of the B/Mo ratio in sublimates collected on Ta metal foil was accomplished by Mr. John Schleicher of the Kansas Geological Survey who studied spectrographically, in emission, samples and bracketing standards both of which had been prepared similarly by K_2CO_3 - KNO_3 (90-10 by wt.) fusion.

The identification of solid phases in reaction products or on the surface of evaporation specimens was performed effectively and quickly with the spectrogoniometer attachment of the GE XRD-3D X-ray diffraction apparatus fitted with a Cu tube and Ni filter.

Apparatus.-- The steel dies were similar to those previously reported⁷. The experiments were performed in a vacuum line having

(7). E.D. Eastman, Leo Brewer, LeRoy A. Bromley, Paul W. Gilles and Norman L. Lofgren., J. Am. Ceram. Soc. 34, 128 (1951)

the laboratory designation, Apparatus No. 2, which is described elsewhere⁸. It consisted of oil mechanical and diffusion pumps,

(8) Paul W. Gilles, Thomas A. Milne, Bernard D. Pollock, and Quentin de L. Wheatley, (to be published).

appropriate glass, silica, and metal vacuum containers, vacuum gauges, an optical window, and induction furnace work coil. The pumps evacuated the system to a pressure of 10^{-5} mm, as determined by an ion gauge and by a cold cathode ion gauge, before heating and did not permit the pressure to rise about 10^{-4} mm while the samples were hot. Usually the pressure was between 3×10^{-6} and 10^{-5} mm. High frequency power was supplied by an Ajax 6-kw spark gap converter to the work coil which surrounded that part of the vacuum system containing the sample. Temperatures were measured by sighting a disappearing filament optical pyrometer, which had been certified by the NBS, into the blackbody hole in the sample. The precision with which the brightness of the filament could be matched to that of the sample at 1800 to 2000°C was about $\pm 5^\circ$, and absolute temperatures were subject to a probable error of $\pm 15^\circ$.

Procedure.-- Preceding each vaporization experiment the sample was heated to a temperature at least as great as that desired for the experiment to accomplish outgassing and purification. In all of the vaporization experiments, except those with MoB-MoB₂ samples, the cylinders were surrounded by a cylindrical Ta shield that served both as insulation and as a collector for the subliming vapor. During the heatings the cylinder was supported by a slotted graphite plate and was covered by a second slotted graphite plate. These plates had two purposes: to reduce, to negligible amounts, the mass loss from the ends; and to maintain a more nearly even temperature distribution throughout the sample by reducing the heat losses from the ends. The graphite plates did not warp as would have thin metal plates when the latter reacted with the sample.

The measurements included the time and temperature of the run,

the sample dimensions, the sample weight before and after the run, the X-ray diffraction pattern, the Ta shield wt. gain, and the analysis of the sublimate. The runs lasted from 15 min. to 5 hrs.

RESULTS

The Evaporation of $\text{Mo}_2\text{B(s)}$.-- To determine whether Mo_2B is a constant vaporizing composition in a Langmuir experiment, a pure Mo_2B cylinder was subjected to the following sequence of operations: X-ray study of surface composition, vacuum evaporation for 45 min. at 1815°C , X-ray study of surface, removal of surface layer by grinding, X-ray study, vacuum evaporation for 50 min. at $2000\text{--}2050^\circ\text{C}$, X-ray study, removal of surface layer by grinding, X-ray study, vacuum evaporation for 30 min. at $2000\text{--}2035^\circ\text{C}$, X-ray study, vacuum evaporation for 2 hrs. at 2075°C , X-ray study.

At the beginning of the sequence and after each grinding, the X-ray examinations showed that the surface of the cylinder was predominantly Mo_2B . Following each evaporation, the surface was principally Mo with only small amounts of Mo_2B ; and following the last two heatings, which totaled 2.5 hrs. and which were not separated by a grinding, only Mo was found on the surface.

The formation of Mo in these experiments shows that in a Langmuir evaporation, $\text{Mo}_2\text{B(s)}$ loses B at a rate faster than one-half that of Mo, and therefore Mo_2B does not vaporize, in this kind of experiment, to give a gas of the same composition.

The Reaction $\text{Mo}_2\text{B(s)} = 2\text{Mo(g)} + \text{B(g)}$.-- The data in Table I were obtained in experiments with three different cylinders, fabricated from material synthesized to have a composition in the MoB phase region. X-ray examination of the cylinders after the

Table I

Experimental Data for the Reaction $\text{Mo}_2\text{B(s)} = 2\text{Mo(g)} + \text{B(g)}$

Sample Loss, mgms	46.9	43.8	19.2	20.9	33.2	32.6	49.5	44.1
Shield Gain, mgms	40.7	40.7	13.3	18.1	29.2	26.9	43.3	39.3
Initial Area, cm^2	8.49	7.99	8.40	8.30	8.22	8.63	8.41	8.16
Mean Temp., $^{\circ}\text{K}$	2377	2374	2234	2237	2332	2331	2325	2311
Time, Seconds	5800	6420	12,840	19,800	7620	7080	14,400	15,000
Sublimate Analysis Wt. Fraction Boron	0.16	0.18	0.17	0.17	0.19	0.14	0.21	0.24
P_{B} , (10^{-8} atm)	4.42	4.76	0.671	0.605	2.92	2.03	2.48	2.54
P_{Mo} , (10^{-8} atm)	7.77	7.27	1.11	0.998	4.18	4.20	3.13	2.70
$K_1 = (P_{\text{B}})(P_{\text{Mo}})^2$ (10^{-24} atm ³)	266	252	0.826	0.603	51.0	35.8	24.3	18.5
$-\text{Log } K_1$	21.575	21.599	24.083	24.226	22.296	22.450	22.614	22.737
$-\frac{\Delta F^{\circ} - \Delta H_{298}^{\circ}}{T}$	102.3	102.3	103.4	103.4	102.7	102.7	102.7	102.7
ΔH_{298}°	478.0	477.6	477.4	479.6	477.6	479.0	479.6	477.9

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experiments indicated that the surface was Mo_2B and the core was the MoB phase.

The previously demonstrated fact that Mo_2B is not a constant subliming composition in a Langmuir experiment and the absence of Mo(s) and persistence of $\text{Mo}_2\text{B}(s)$ on the surface in the present experiments are reconciled as follows: at high temperature, after some loss of B had occurred, the cylinders consisted of a surface of Mo_2B , an intermediate region of Mo_3B_2 and a core of the MoB phase, the last two of which acted as sources of B which diffused to the surface and there caused the pressure of B(g) to be larger than at the surface on a Mo_2B cylinder. This supply of B caused the Mo(g) pressure to be below the vapor pressure of Mo(s), and therefore solid Mo did not appear.

Under such circumstances the most appropriate reaction, at the surface is,

and the treatment of the data in Table I is on this basis.

The first two runs shown in Table I were performed with one cylinder, the next three with another, and the last three with a third.

The first row in Table I gives the wt. loss from the cylinders and their graphite end plates; the second row gives the wt. gain of the shield-collector; the third row gives the sample evaporating area; i.e., the curved cylindrical area; the fourth row contains the corrected temperature and the fifth row the effective time, both obtained from plots of temp. vs. time. The probable error in the temp. is estimated to be $\pm 15^\circ\text{K}$. and in the time $\pm 2\%$.

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The sixth row contains the results of the spectrographic analyses of the sublimates collected on the Ta shield-collector. These analyses together with the weights of the deposits have been used in the Langmuir expression with an accommodation or condensation coefficient of unity to obtain the partial pressures of B and Mo as shown in the next two rows. The wt. gain of the shield is taken as more representative of the evaporation rate than is the sample loss, because of the leakage out of the black body holes and additional vaporization of non-condensable impurities from the sample. Auxilliary experiments, in which B was sublimed, indicated that the "gettering" of B(g) by hot Ta was nearly complete. If sample wt. losses were used instead of the collector wt. gains the conclusions would not be significantly different.

From the pressures so obtained, the equilibrium constant and its logarithm have been calculated in the usual way. For reactions in which only solids are involved, ΔS and ΔC_p are close to zero, and, in the absence of thermal data, we have taken them to be zero for the formation of Mo_2B from its solid elements. The change in the free energy function, $(\Delta F^\circ - \Delta H_{298}^\circ)/T$, for reaction (1) is then twice the difference in the free energy functions for Mo(g) and Mo(s) plus the difference in the free energy function for B(g) and B(s). Values of these quantities for B have been obtained from the tables of Brewer⁹ and values for Mo given by

(9) Leo Brewer, The Thermodynamic and Physical Properties of the Elements. The Chemistry and Metallurgy of Miscellaneous Substances: Thermodynamics, edited by Laurence L. Quill, National Nuclear Energy Series, Division IV- Plutonium Project Record, Vol. 19B, paper 3, pp. 13-39, McGraw-Hill, New York (1950).

Edwards, Johnston, and Blackburn¹⁰ have been changed to a

(10) J.E. Edwards, H.L. Johnston, and P.E. Blackburn, This Journal 74, 1539 (1952).

reference temp. of 298°K by the use of a value of 394 cal. for $\Delta H_{298}^{\circ} - \Delta H_0^{\circ}$ for the evaporation of Mo, taken from Brewer⁹ and Simon and Zeidler¹¹.

(11) F. Simon and W. Zeidler, Z. physik. Chem. 125, 383 (1926).

Values of the desired heat for the reaction (1) given in the last row were obtained by a combination of the values from the two previous rows. The average of these values, $\Delta H_{298}^{\circ} = 478.3$, may be used together with the heat of sublimation of Mo as determined by Edwards, Johnston, and Blackburn¹⁰, corrected to a standard temperature of 298°K, $\Delta H_{298}^{\circ} = 155.94 \pm 0.20$ kcal/mol, and the heat of sublimation of B, $\Delta H_{298}^{\circ} = 140.9 \pm 2.0$ kcal/mol., as determined by Searcy and Myers¹², to obtain the heat of

(12) Alan W. Searcy and Clifford E. Myers, The Heat of Sublimation of Boron, The Dissociation Energy of BO Gas, and The Gaseous Species of the Boron-Boric Oxide System, Sixth Technical Report, Contract No. N7 onr-394/12 Project No. Nr-032-331, Purdue University, June 1953.

formation of $\text{Mo}_2\text{B(s)}$ as $\Delta H_{298}^{\circ} = -25.5$ according to the reaction,

$$2 \text{ Mo(s)} + \text{B(s)} = \text{Mo}_2\text{B(s)} \quad (2)$$

An estimate of the probable error of these two heats may be in the following way. An examination of the data for Cr_3C_2 and TiC indicate that for the reactions yielding these substances from

the elements, the change in the free energy function at 1500°K is within three units of zero. The assumption made in this paper is that the free energy function change is zero for solid reactions and if this is in error by 2 a.u., the heats reported are in error by 4.6 kcal. per mol. If the equilibrium constants are in error by a factor of two, the heats are in error by 3.2 kcal. per mol, and if the temperature is in error by 15°K, the heats are in error by 3.0 kcal. per mol.

In the light of these uncertainties, we take as the probable errors in ΔH_1 and ΔH_2 a value of ± 6 kcal/mol, even though the p.e. calculated from the experimental data, alone, is only 0.2 kcal/mol.

The Reaction $\text{Mo}_2\text{B(s)} = 2\text{Mo(s)} + \text{B(g)}$.-- The data in Table II were obtained with one cylinder that was initially pure Mo_2B . As pointed out earlier, these experiments produced Mo(s) , and under these circumstances the most appropriate reaction, at the surface, is

and the treatment of the data in Table II is on this basis. The first two experiments shown are the same ones that concluded the sequence of operations, discussed earlier, leading to the conclusion that the Mo_2B is not a constant vaporizing composition in a Langmuir experiment. The other two were performed subsequently. At the beginning of each run, Mo_2B , at least, was present; and at the end of the runs, except for the second, both Mo_2B and Mo were present, according to the X-ray examinations. Thus, these experiments give the data applicable to reaction (3).

In Table II, the first five rows have the same significance as these in Table I. The wt. changes are probably accurate to

TABLE II
Experimental Data for the Reaction $\text{Mo}_2\text{B(s)} = 2\text{Mo(s)} + \text{B(g)}$.

Sample loss (mgms)	12.7	45.3	6.1	4.3
Shield gain (mgms)	6.3	39.7	5.2	3.5
Temp. ($^{\circ}\text{K}$)	2310	2350	2260	2245
Area (cm^2)	7.7	7.6	7.2	7.1
Time (sec.)	1600	7260	3600	2940
P_{Mo}° (10^{-8}atm)	4.32	7.22	2.20	1.82
Mo wt. loss (calc)(mgms)	4.9	35.9	5.2	3.5
$K_3 = P_{\text{B}}$ (obs)(10^{-8}atm)	3.8	2.3	-	-
$K_1 = P_{\text{Mo}}^2 \times P_{\text{B}}$ (10^{-24}atm^3)	18	110	1.8	0.87
$K_3 = K_1 / (P_{\text{Mo}}^{\circ})^2$ (calc)(10^{-8}atm)	1.0	2.1	0.37	0.26
$P_{\text{B}} / P_{\text{Mo}}^{\circ}$	0.23	0.29	0.17	0.15

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about 20% in the last runs. The sixth row contains the vapor pressure of Mo calculated from the data of Edwards, Johnston, and Blackburn¹⁰, and these values are used in the Langmuir equation to calculate the wt. loss of the sample arising from the evaporation of Mo alone, shown in the seventh row. For the latter calculation the area was taken to be the total evaporating area as given in the fourth row.

A comparison of the values in the second, and seventh rows shows that substantially all the wt. loss can be accounted for by evaporation of Mo alone, thus indicating that the boron wt. loss is probably considerably smaller than the Mo wt. loss. For the first two experiments, it is possible to obtain, by difference, a wt. loss of B, and from it to calculate P_B given in the eighth row. Because the Langmuir expression contains molecular weight terms; the pressures, number of moles evaporating, and masses evaporating for the two species, B and Mo, are related according to the expression,

$$\frac{P_B}{P_{Mo}} = \left(\frac{M_B}{M_{Mo}} \right)^{1/2} \frac{n_B}{n_{Mo}} = \left(\frac{M_{Mo}}{M_B} \right)^{1/2} \frac{m_B}{m_{Mo}} \quad (4)$$

If we attribute to B a wt. loss in these experiments less than about one-third that of Mo, then $P_B < P_{Mo}^0$.

On the other hand, it has been shown by the appearance of Mo(s) that the number of moles of B lost is greater than 1/2 that of Mo, whence $P_B > 0.168 P_{Mo}^0$.

From the reaction (1) and its equilibrium constant, obtained previously, it is possible to calculate P_B in the Mo-Mo₂B region in the following way: Since K_1 gives simultaneously occurring values for P_B and P_{Mo} in equilibrium with Mo₂B(s); when $P_{Mo} = P_{Mo}^0$,

as it is in the Mo-Mo₂B region, P_B is given by $K_1 / (P_{Mo}^o)^2$. Values of K_1 obtained from reaction (1) are listed in the ninth row and are used with values of P_{Mo}^o in the sixth row to obtain P_B or K_3 listed in the tenth row. These values are consistent with the values in the eighth row to within the experimental weighing error.

The last row contains the ratio of the partial pressures of B and Mo in the Mo-Mo₂B region obtained from the sixth and tenth rows, that is, from calculated Mo vapor pressures and K_1 values obtained from the study of reaction (1). The average of these values, 0.21, is in agreement with the conclusion, $0.168 < P_B / P_{Mo}^o < 1$, obtained from a study of reaction (3); and the consistency indicates that the proper interpretation has been given to both sets of measurements.

Analyses of the sublimates obtained in the study of reaction (3) were not made.

The Reaction $2MoB_{0.96}(s) = Mo_2B(s) + 0.92B(g)$.-- The data in Table III were obtained in experiments with the same cylinder used for the third, fourth, and fifth experiments in Table I. Although the present experiments were carried out with a different purpose in mind, the same sample was used because of the purity it had attained by virtue of its previous heating. The surface of Mo₂B was removed by grinding so that the MoB phase was exposed. The cylinder was then outgassed for about 5 min. at 1700-1800°C., during which a wt. loss of about 2 to 3 mgms. occurred, and then was weighed just before the vaporization experiment.

For these experiments the temperatures were kept low enough to preclude the existence of Mo₃B₂ and X-ray examination showed

Table III

Experimental Data for the Reaction $2 \text{MoB}_{0.96}(\text{s}) = \text{Mo}_2\text{B}(\text{s}) + 0.92\text{B}(\text{g})$

Sample loss (mgms)	1.0	1.0	0.9	1.4
Shield gain (mgms)	0.6	0.8	0.9	1.1
Area (cm^2)	8.1	8.1	8.0	7.8
Time (sec)	1080	1200	900	3300
Temp. ($^{\circ}\text{K}$)	2103	2098	2161	2084
P_{B} (obs) (10^{-8} atm)	2.1	2.6	3.9	1.3
P_{B}° (10^{-8} atm)	13	12	30	9.2
$P_{\text{B}}/P_{\text{B}}^{\circ}$	0.16	0.22	0.13	0.14
$\frac{\Delta F^{\circ}}{T} = -0.92R \ln P_{\text{B}}$	32.4	31.9	31.2	33.2
ΔH_{298}°	136.3	134.9	137.4	136.7

that the heatings were terminated before the $\text{MoB}_{0.96}$ had completely disappeared from the surface. Under these circumstances, the reaction at the surface containing Mo_2B and $\text{MoB}_{0.96}$ is most appropriately,

and the data in Table III are interpreted on this basis.

The first five rows have the same significance as before. It should be noted that the wt. changes are small and therefore subject to large errors. The sublimates could not be analyzed. The observed B pressures in the sixth row have been obtained from the shield wt. gain by attributing the entire wt. gain on the shield to B. The vapor pressures of elemental B given in the seventh row have been calculated from the data of Searcy and Myers¹². The ratio of these pressures is given in the eighth row.

The values for K_1 , in the temperature range of these experiments, are about 10^{-27} , and combination of this value with the observed B pressure indicates that P_B/P_{Mo} in the Mo_2B - $\text{MoB}_{0.96}$ region is 30 or larger, and therefore the assumption that the entire weight gain was B, is justified.

The ninth row contains the values of $\Delta F^\circ/T$ for reaction (5) calculated from the equilibrium constant thereof, $K_5 = (P_B)^{0.92}$. In the tenth row are given values of ΔH_{298}° for reaction (5) calculated from the values in the preceding row by the same procedure as that used for reaction (1). The average of these values, 136.3 kcal/mol, which is taken as the best value for the heat of reaction (5), may be used together with the heat of reaction (2) and the heat of sublimation of B to obtain the heat of formation of $\text{MoB}_{0.96}(\text{s})$ as $\Delta H_{298}^\circ = -16.1$ kcal/mol according to the reaction,

In the calculation of heat for reaction (5), errors in the temperature are less important than they were in connection with reaction (1), and we take ± 5 kcal/mol as the p.e. for the heats of reaction (5) and (6).

The Reaction $\text{MoB}_{2.14}(\text{s}) = \text{MoB}_{1.06}(\text{s}) + 1.08 \text{ B}(\text{g})$.-- The data in Table IV were obtained in an experiment with five small samples, having initial compositions shown in the first row, that had been prepared by heating powder mixtures in silica. After an outgassing run in a Mo crucible for an hour at 1825°C , the samples were heated in a Mo crucible for 5000 sec. at 2159°K . Each sample was suspended by a Mo wire and was surrounded by a cylinder of 0.002" Mo sheet. These shields cast sharp shadows and it was assumed that these experiments could be considered as Langmuir ones. No analyses were made.

The fifth row contains B pressure calculated from the wt. losses by assuming the entire wt. loss to be B.

After the experiment the first three samples were uniformly grey in color and the last two were grey on the outside and blue-black inside. X-ray examination showed the grey phase to be the MoB one and the blue-black phase to be the Mo_2B_5 one. It is apparent that the latter phase decomposes to the former by giving off B(g) at a rapid rate. The value calculated from the last experiment, 0.9×10^{-7} atm, may be considered a lower limit for the partial pressure of B in equilibrium with $\text{MoB}_{1.06}$ and $\text{MoB}_{2.14}$ according to the reaction,

An upper limit may be taken as the vapor pressure of B, which, from the data of Searcy and Myers¹², is about 2.8×10^{-7} atm. We estimate that the B pressure in reaction (7) is one-half the B vapor pressure or 1.4×10^{-7} atm at 2159°K .

Table IV

Experimental Data for the Reaction $\text{MoB}_{2.14}(\text{s}) = \text{MoB}_{1.06}(\text{s}) + 1.08\text{B}(\text{g})$

Initial B/Mo (synthesis)	1.0	1.3	1.5	1.8	2.2
Initial wt. (gm)	0.3178	0.3798	0.3084	0.2504	0.2101
Wt. Loss (mgm)	0.1	0.2	0.4	1.0	2.0
Area (cm^2)	1.5	1.7	1.6	1.5	1.4
P_B (10^{-8} atm)	0.4	0.7	2	4	9
$\frac{\Delta F^\circ}{T} = -1.08 \ln P_B$	41.5	40.5	38.1	36.5	34.8
ΔH°_{298}	172	170	165	161	157

From this value and assumptions similar to those made earlier, the heat for reaction (7) becomes $\Delta H_{298}^0 = 155.3 \pm 6$ kcal/mol. Before a heat of formation for $\text{MoB}_{2.14}(\text{s})$ may be calculated, the heat of formation of $\text{MoB}_{1.06}(\text{s})$ must be obtained. This is accomplished in the following section.

The Solid Solution $\text{MoB}_{0.96-1.06}$ -- From the data given for reactions (5) and (7) and the usual assumption regarding the free energy functions, the B pressures in equilibrium with $\text{Mo}_2\text{B}(\text{s})$ and $\text{MoB}_{0.96}(\text{s})$ and with $\text{MoB}_{1.06}(\text{s})$ and $\text{MoB}_{2.14}(\text{s})$ may be calculated for any temperature. At 2200°K. these values are 9.4×10^{-8} and 2.5×10^{-7} atm., respectively. How P_B changes through the MoB phase from the first of these values to the second is not known, but Darken and Gurry¹³, in their studies of the Fe-O system found

(13) L. S. Darken and R. W. Gurry, This Journal 67, 1398 (1945); 68, 798 (1946).

that $\log P_{\text{O}_2}$ changed linearly with the atomic ratio O/Fe in the liquid oxide and their graphs show a similar behavior for the solid wüstite region. If we assume that the Mo-B system behaves similarly, we write,

$$\log P_B = k \left(\frac{N_B}{N_{\text{Mo}}} \right) + c \quad (8)$$

in which N_B/N_{Mo} is the atomic ratio B/Mo in the solid, and in which the constants k and c may be calculated from the above pressures to have the values 4.30 and -11.16 at 2200°K.

For the single phase MoB condensed region, the Gibbs-Duhem equation in the form,

$$d \ln P_{\text{Mo}} = - \frac{N_B}{N_{\text{Mo}}} d \ln P_B, \quad (9)$$

is applicable and permits the calculation of P_{Mo} .

Integration of equation (9) following substitution from equation (8) yields

$$\log \frac{(P_{\text{Mo}})_{1.06}}{(P_{\text{Mo}})_{0.96}} = -\frac{k}{2} \left[\frac{N_{\text{B}}}{N_{\text{Mo}}} \right]_{0.96}^{1.06} \quad (10)$$

in which the pressures of Mo on the left are those in equilibrium with $\text{Mo}_2\text{B}-\text{MoB}_{0.96}$ and $\text{MoB}_{1.06} - \text{MoB}_{2.14}$.

This equation and the value of k at 2200°K indicate that the ratio of Mo pressures appearing in equation (10) is 0.37 at 2200°K . As was shown in the section on reaction (5) the partial pressure of Mo in equilibrium with Mo_2B and $\text{MoB}_{0.96}$ may be calculated from P_{B} in this region and K_1 . At 2200°K , P_{Mo} so obtained is 1.2×10^{-9} atm, whence the partial pressure of Mo in equilibrium with $\text{MoB}_{1.06}$ and $\text{MoB}_{2.14}$ is 4.4×10^{-10} atm.

To see whether this calculated pressure of Mo is very sensitive to the assumed manner in which P_{B} changes with composition, P_{Mo} values were calculated from two different assumptions: (1) that the partial pressure of B itself, not its logarithm, varies linearly with atomic ratio, and (2) that P_{B} varies linearly with the mole fraction of B. Because the values obtained from these three treatments were insignificantly different, it is concluded that the one calculated first is satisfactory.

It can easily be shown that these values of P_{B} and P_{Mo} at the extreme ends of the MoB solid solution indicate the heat of formation of $\text{MoB}_{1.06}$, according to the reaction,

to be 0.5 kcal more negative than that for $\text{MoB}_{0.96}$, according to reaction (6). Thus, $\Delta H_{298}^\circ = -16.6 \pm 5$ kcal/mol for reaction (11).

From the heats for reactions (7) and (11) and the heat of sublimation of 1.08 moles of B, the heat of formation of $\text{MoB}_{2.14}$,

according to the reaction,

may be calculated to be $\Delta H_{298}^{\circ} = -19.7 \pm 8 \text{ kcal/mol}$.

The Solid Solution $\text{MoB}_{2.14-2.33}$ --- How P_B changes across the second solid solution is also not known, but the assumption of equation (8) may again be made. Since beyond $\text{MoB}_{2.33}$, $P_B = P_B^{\circ} = 5.0 \times 10^{-7} \text{ atm}$. at 2200°K , k and c have the values 1.58 and -9.98. The use of equation (10) with 2.33 and 2.14 replacing 1.06 and 0.96, and with $P_{\text{Mo}} = 4.4 \times 10^{-10} \text{ atm}$. just calculated for the $\text{MoB}_{1.06} - \text{MoB}_{2.14}$ region, gives for the partial pressure of Mo in equilibrium with $\text{MoB}_{2.33}(\text{s})$ and B(s) , a value of $9.5 \times 10^{-11} \text{ atm}$. at 2200°K .

It can be shown, in the same fashion used for MoB, that the values of the partial pressures at the two ends of the $\text{MoB}_{2.14-2.33}$ solid solution indicate the heat of formation of $\text{MoB}_{2.33}$, according to the reaction,

to be 0.3 kcal more negative than that for $\text{MoB}_{2.14}$, according to reaction (12). Thus, $\Delta H_{298}^{\circ} = -20.0 \pm 8 \text{ kcal/mol}$ for reaction (13).

The Compound Mo_3B_2 --- An approximate value for the heat of formation of Mo_3B_2 according to the reaction,

may be obtained in the following way. Since the compound is stable at high temperature but not at room temperature, ΔF° for the disproportionation reaction,

must be close to zero.

If Mo_3B_2 is assumed to be on the verge of stability at 298°K, i.e. $\Delta F_{298}^{\circ} = 0$ for reaction (15), and if ΔS and ΔC_p are assumed zero, as before, for solid reactions; then $\Delta H_{298}^{\circ} = 0$ for reaction (15). The heat of formation according to reaction (14) is then, $\Delta H_{298}^{\circ} = -41.9 \pm 10$ kcal/mol.

DISCUSSION

Heats of Formation.-- The values for the heats of formation of the various compounds in the Mo-B system are summarized in Table V.

Table V

Composition	ΔH_{298}° (kcal/mol)
$\text{Mo}_2\text{B}(\text{s})$	-25.5 ± 6
$\text{Mo}_3\text{B}_2(\text{s})$	-41.9 ± 10
$\text{MoB}_{0.96}(\text{s})$	-16.1 ± 5
$\text{MoB}_{1.06}(\text{s})$	-16.6 ± 5
$\text{MoB}_{2.14}(\text{s})$	-19.7 ± 8
$\text{MoB}_{2.33}(\text{s})$	-20.0 ± 8

These values have been obtained from studies of vaporization processes and have been calculated by assuming (1) that ΔS and ΔC_p for reactions involving only solids are both zero, and (2) that the heat of sublimation of Mo^{10} and B^{12} at 298°K are 155.94 ± 0.20 and 140.9 ± 2.0 kcal/mol.

The values in Table V show that for the reaction,

$\Delta H_{298}^{\circ} = 8.4$ kcal a value consistent with the previously known stability of Mo_2B with respect to disproportionation.

Equilibrium Pressures of $\text{B}(\text{g})$ and $\text{Mo}(\text{g})$ and the Evaporation of Mo_2B .-- Fig. 1 shows the partial pressures of $\text{B}(\text{g})$ and $\text{Mo}(\text{g})$ at 2200°K in the different regions of the diagram. The three

compounds shown are Mo_2B , $\text{MoB}_{0.96-1.06}$, and $\text{MoB}_{2.14-2.33}$. The horizontal lines occur, of course, in the regions of two solid phases. The values in these invariant regions at constant temperature have been calculated earlier, and the dashed lines indicate the variation of the pressures over the solid solutions.

If Mo_3B_2 is just barely stable with respect to disproportionation at 2200°K , a vertical line might be drawn in the diagram at the appropriate value of the abscissa, but the partial pressure of each gas would be the same on both sides of such a line.

It is clear from Fig. 1 that all higher molybdenum borides decompose to Mo_2B with loss of B(g) in vacuum at high temperatures. It has previously been pointed out that Mo_2B , itself, decomposes in a Langmuir type experiment to give Mo(s) because the partial pressure of B(g) is greater than 0.168 times the partial pressure of Mo . For Knudsen effusion, the relationships are the same as in the Langmuir technique and, therefore, Mo_2B would also decompose in this type of experiment. In other words, Mo_2B does not evaporate in these types of experiments to give a gas of the same composition and is not, therefore, a constant subliming composition in these experiments.

In a closed system, however, containing pure stoichiometric $\text{Mo}_2\text{B(s)}$ initially, the gas and solid that are present ultimately in equilibrium with each other will have the same composition, Mo_2B ; the partial pressure of Mo will be twice that of B ; and $P_{\text{Mo}} = (2K_1)^{1/3}$. To see the reason for this behavior, notice that to the left of Mo_2B in Fig. 1, P_{Mo} is greater than twice P_{B} , and to the right, P_{B} is much greater than P_{Mo} . In a system containing Mo_2B and a vanishingly small quantity of Mo(s) , the latter, in the

attempt of the system to produce the higher pressure of Mo, will entirely vaporize, thus leaving only Mo_2B in the solid. Similarly a vanishingly small amount of $\text{MoB}_{0.96}$, in the attempt of the system to produce the much higher pressure of B, will entirely decompose to Mo_2B , thus producing a single solid phase.

In experiments, then, in which the vapor is not allowed to escape, compositions just above and below Mo_2B yield systems containing only this solid, and therefore in such experiments with pure $\text{Mo}_2\text{B(s)}$, no other solid can appear. Since Mo_2B has a negligible solid solution range, the composition of solid may not, according to the above argument, change, and, therefore, the gas arising from it must have the same composition.

Furthermore, if it were possible to carry out a vaporization experiment at pressures sufficiently high so that only the pressures and not the molecular weights were important, Mo_2B would be a constant subliming composition. Because of the proximity of the melting point, however, such a situation cannot be realized in the solid. Whether or not there is a constant vaporizing composition in the liquid is not certain.

The Existence of Gaseous Molecules.-- The dissociation energy of $\text{B}_2(\text{g})$ of 3.6 e.v. given by Herzberg¹⁴ can be used to show that

(14) G. Herzberg, Spectra of Diatomic Molecules, p. 506, D. Van Nostrand Co., New York, 1950.

at the temperatures and the pressures of B(g) encountered in these experiments, the partial pressure of $\text{B}_2(\text{g})$ is entirely negligible. Therefore our assumption throughout the work that B(g) is the only gaseous species of that element is justified. There is no evidence for any molecular species of Mo.

In addition to the absence of reports on gaseous borides, two kinds of arguments can be used to show that gaseous borides are unimportant in the consideration of the equilibria treated in this paper. If there were a gaseous boride in large concentration in the gas phase, the pressure observed would be higher than that to be expected on the basis of evaporation to the elements. But in the $\text{Mo-Mo}_2\text{B}$ experiments and in the $\text{MoB}_{1.06} - \text{MoB}_{2.14}$ experiments, the measured pressures were close to the vapor pressures of Mo and B respectively and, therefore, did not indicate any gaseous boride. In other words, Fig. 1, which was obtained reasonably directly from the measurements, is exactly the kind of diagram one would expect if vaporization occurred to give atoms only, whereas it would be considerably different if other processes were involved.

The second reason for concluding that there are no stable gaseous borides is as follows. If our vaporizations produce large quantities of gaseous molecules, we obtain no direct information about vaporization producing atoms because the true pressures of atoms would be smaller than the experimentally observed pressures. But low pressures correspond to high heats of vaporization, and therefore the true heats of vaporization would be larger, and the heats of formation of the solid compounds would be more negative than we have reported here. Our values and those of Brewer and Haraldsen¹⁵ agree, however, leading to the conclusion that gaseous

(15) Leo Brewer and H. Haraldsen, (to be published).

molecules must be unimportant in our experiment.

Constant Vaporizing Compositions in Other Boride Systems.--
The difference in the behavior of distinct metal-boron systems, with respect to constant vaporizing compositions, is related, in

the absence of gaseous molecules, to heats of sublimation of the elements and the heats of formation of the compounds. An increase in the stability of the compound relative to the solid elements enhances the possibility for a constant vaporizing composition. If two metals are less volatile than boron, a change from the more volatile to the less volatile one will decrease the possibility of a constant vaporizing composition; but on the other hand, if the metals are more volatile than B, a change from the more volatile to the less volatile one will enhance the possibility.

The stabilities of the refractory borides given by Brewer and Haraldsen¹⁵, the heats of sublimation of the metals, and our observation that Mo_2B is on the verge of being a constant vaporizing composition can be used to indicate which metal-boron systems are likely to show such compositions.

The W-B and Cr-B systems will lose B and Cr, respectively, over the entire range of compositions and will show no such composition. The Ta-B system, also, probably will lose B over the entire range. The Zr-B and Ti-B systems should show constant vaporizing compositions at ZrB or ZrB_2 and TiB_2 . The result for the Ce-B system is uncertain.

We are pleased to acknowledge the support of the Atomic Energy Commission and the helpful conversations and communications with Professors Leo Brewer and Alan W. Searcy and Drs. Robert Steinitz, Frank W. Glaser, and John L. Margrave. We also wish to thank Professor David H. Templeton and Mrs. Carol H. Dauben for their X-ray reports during the early stage of the work, and Mr. Harry E. Robson for help with the calculations in the solid solution regions.

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Fig. 1. Pressures of Mo(g) and B(g) in Equilibrium with the Solid Phases in the Molybdenum-Boron System at 2200° K.

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