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REPORT No. 27/R/59

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Thermodynamic Aspects of the Reactions of Boron Hydrides and Related Compounds

A. J. Owen

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REPORT NO. 27/R/59

Thermodynamic Aspects of the Reactions  
of Boron Hydrides and Related Compounds

by

A. J. Owen

Approved: *A. Lovecy*

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Reference: WAC/91/26

1. SUMMARY

Thermodynamic calculations have been made on the following reactions and systems:

- (i) The thermal decomposition of boron hydrides to boron and hydrogen,
- (ii) The formation of diborane by hydrogenation of a boron halide,
- (iii) The pyrolysis of diborane to higher boron hydrides,
- (iv) Alkylation reactions.

The calculations show that in order to produce diborane from a boron halide and hydrogen, the hydrogen must be in a very active form. The other systems considered consist of reactions which go to completion, with the exception of the equilibria which exists between diborane, tetraborane and/or dihydropentaborane. The probable values of the equilibrium constants of reactions involved in the equilibria have been indicated.

Estimated values of the free energy of formation of alkyl boranes are given in the Appendix.

2. INTRODUCTION

Thermodynamic calculations show that the heats of combustion of compounds containing boron, carbon and/or hydrogen are higher than that of aviation kerosene (1, 2.). Boron hydrides and their derivatives have therefore a potential importance as high energy fuels, and this report deals with the thermodynamic aspects of reactions which may be involved in their synthesis.

Thermodynamic calculations of the equilibria and heats of reaction have been made with the accuracy the available data will allow, all reactions being assumed to occur at a constant pressure of one atmosphere. Thermodynamic data have been taken from the publications of the National Bureau of Standards(3, 4), the work of Bauer (5), and in certain cases estimated by empirical methods.

The reactions have been grouped into four sections under the headings:

- Section 3. The Thermal Decomposition of Diborane and the Higher Hydrides to Boron and Hydrogen.
- Section 4: The Formation of Diborane by Hydrogenation of a Boron Halide. (The use of lithium aluminium hydride is not included, through lack of sufficient thermodynamic data.)
- Section 5. The Pyrolysis of Diborane.
- Section 6. Alkylation Reactions.

/TABLE 1 .....

TABLE 1

Equilibrium Constants and Heats of Reaction for the Thermal  
Decomposition of Boron Hydrides

Reaction	Equilibrium Constants at:				Heat of Reaction, $\Delta H_{298}^{\circ}$ , kcal/mole
	Temperature, K				
	300°	500°	700°	900°	
1. $B_2H_6 \rightleftharpoons 2B + 3H_2$	$2.94 \times 10^{14}$	$3.70 \times 10^{12}$	$1.02 \times 10^{12}$	$6.01 \times 10^{11}$	-7.53
2. $B_4H_{10} \rightleftharpoons 4B + 5H_2$	$1 \times 10^{30}$	-	-	-	-13.9
3. $B_5H_{11} \rightleftharpoons 5B + 5\frac{1}{2}H_2$	$3 \times 10^{36}$	-	-	-	-16.5
4. $B_5H_9 \rightleftharpoons 5B + 4\frac{1}{2}H_2$	$5.73 \times 10^{28}$	$6.89 \times 10^{24}$	$2.16 \times 10^{23}$	$8.20 \times 10^{22}$	-15.0
5. $B_{10}H_{14} \rightleftharpoons 10B + 7H_2$	$7.31 \times 10^{51}$	$6.29 \times 10^{44}$	$2.86 \times 10^{42}$	$2.24 \times 10^{41}$	-27.0

/3. ....

3. THE THERMAL DECOMPOSITION OF DIBORANE AND THE HIGHER HYDRIDES TO BORON AND HYDROGEN

The thermal decomposition of boron hydrides to boron and hydrogen has been considered first, since these reactions should be included in all thermodynamic calculations of systems in which the hydrides are involved. Over a wide temperature range of 300°K (27°C) to 900°K (627°C) the equilibrium state is that decomposition to boron and hydrogen is virtually complete. For example, the equilibrium constant for the reaction



is greater than  $1 \times 10^{11}$  at 900°K. Table 1 summarizes the equilibrium constants and heats of reaction for these thermal decompositions. It can be seen that all the decomposition reactions are exothermic.

In practice however, none of the hydrides decomposes spontaneously to boron and hydrogen at room temperature. For example, diborane can be stored at room temperature for several days with only slight decomposition (6); the higher hydrides and hydrogen, not boron, are produced, and even at 300°C a nonvolatile solid boron hydride is formed. For complete decomposition to boron and hydrogen, temperatures above 700°C are required (8).

Since all the subsequent calculations were made at temperatures of 327°C or below, the decomposition of the boron hydrides has been neglected in the consideration of the other systems.

4. THE FORMATION OF DIBORANE BY THE HYDROGENATION OF A BORON HALIDE

4.1 Introduction

The first synthesis of diborane by the reduction of a boron halide was carried out in 1931 by Schlesinger and Burg (8), who passed boron trichloride and hydrogen at 10 mm. Hg pressure through an electrical discharge and obtained an overall yield of 15 per cent diborane. Stock and Sutterlin (9) in 1934 used boron tribromide and obtained similar yields. More recently, Hurd (10) has shown that a boron halide, with hydrogen and a hydride of an alkali (or alkaline earth) metal yield diborane. Aluminium has also been used in place of the metal hydride (11).

Thermodynamic calculations have been made on the following systems:

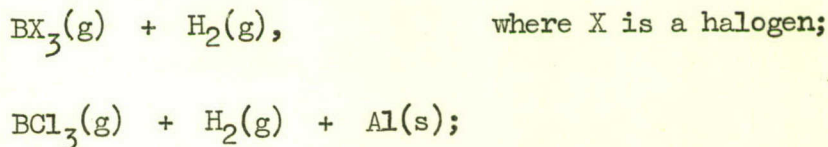


Table 2, p. 4 summarizes the equilibrium constants and heats of reaction for reactions included in the systems.

/TABLE 2 .....

TABLE 2

Equilibrium Constants and Heats of Reaction for Reactions  
Involving the Hydrogenation of Boron Trihalides

Reaction	Equilibrium Constants at:				Heats of Reaction $\Delta H_{300}^{\circ}$ , kcal/mole
	Temperature, K				
	300°	400°	500°	600°	
6. $2\text{BCl}_3 + 6\text{H}_2 \rightleftharpoons \text{B}_2\text{H}_6 + 6\text{HCl}$	$6.85 \times 10^{-52}$	$3.99 \times 10^{-39}$	$4.55 \times 10^{-32}$	$2.72 \times 10^{-26}$	+69.31
7. $2\text{BCl}_3 + 5\text{H}_2 \rightleftharpoons \text{B}_2\text{H}_5\text{Cl} + 5\text{HCl}$	$\sim 1 \times 10^{-44}$	-	-	-	-
8. $6\text{B}_2\text{H}_5\text{Cl} \rightleftharpoons 5\text{B}_2\text{H}_6 + 2\text{BCl}_3$	$\sim 1 \times 10^5$	-	-	-	-
9. $\text{B}_2\text{H}_6 + \text{HCl} \rightleftharpoons \text{B}_2\text{H}_5\text{Cl} + \text{H}_2$	$\sim 1 \times 10^7$	-	-	-	-
11. $2\text{BBr}_3 + 6\text{H}_2 \rightleftharpoons \text{B}_2\text{H}_6 + 6\text{HBr}$	$1.17 \times 10^{-40}$	$5.63 \times 10^{-30}$	$6.71 \times 10^{-24}$	$4.21 \times 10^{-22}$	+54.10
12. $2\text{Al} + 6\text{HCl} \rightleftharpoons 2\text{AlCl}_3 + 3\text{H}_2$	$1 \times 10^{120}$	-	-	-	-200

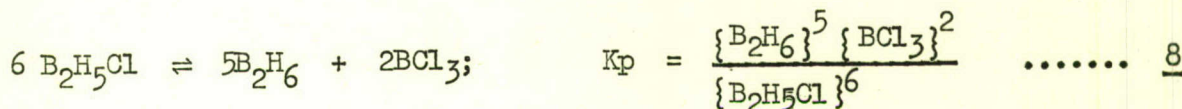
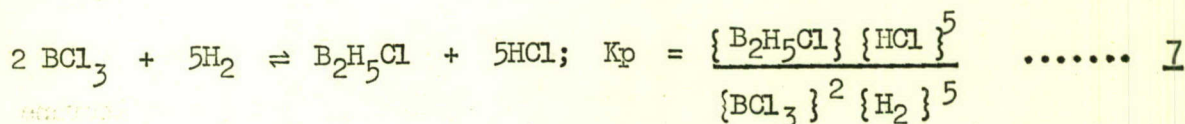
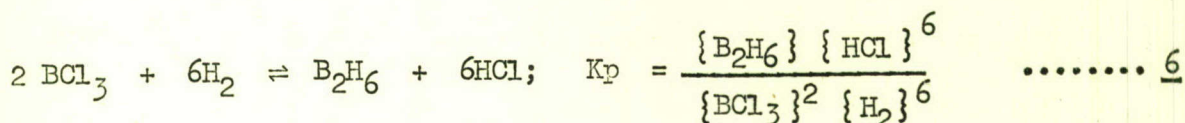
/42 .....

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4.2 System 1:  $\text{BCl}_3(\text{g}) + \text{H}_2(\text{g}); \text{BBr}_3(\text{g}) + \text{H}_2(\text{g})$ .

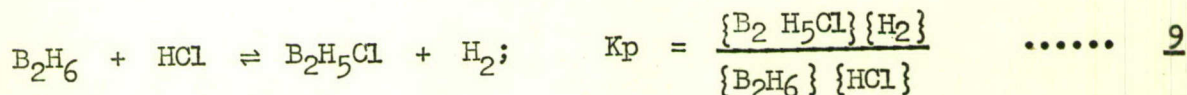
When boron trichloride reacts with hydrogen in an electric arc discharge, the main product is monochlorodiborane, together with hydrogen chloride and small amounts of diborane, (Table 2, opposite).

The reactions that have been chosen to represent this system are:



Note. Here and below  $\{\text{B}_2\text{H}_6\}$  is used to denote "partial pressure of  $\text{B}_2\text{H}_6$ ".

The equilibrium constant for reaction 6 varies between  $6.85 \times 10^{-52}$  at  $300^\circ\text{K}$  and  $2.72 \times 10^{-26}$  at  $600^\circ\text{K}$ , clearly showing that only very low yields of diborane should be expected. Schlesinger and Burg however, found that 15 per cent yields of the diborane/monochlorodiborane mixture could be obtained in an electrical discharge apparatus. In attempting to explain this discrepancy, the free energy of monochlorodiborane was estimated using the equilibrium constant experimentally measured by Stock (12) for the decomposition of monochlorodiborane (reaction 8). The equilibrium constant of  $1 \times 10^5$  leads to a free energy value for monochlorodiborane of  $-13.4$  kcal/mole. A less accurate value of  $-10$  kcal/mole has also been estimated, from the rough experimental equilibrium constant of  $3 \times 10^5$  (12) for the reaction



Using the free energy value of  $-13.4$  kcal/mole, the equilibrium constant for the reaction of boron trichloride and hydrogen to give monochlorodiborane has been estimated at  $300^\circ\text{K}$  to be  $1 \times 10^{-44}$ ; that is, very little monochlorodiborane is predicted at room temperature. Even at  $600^\circ\text{K}$  the equilibrium constant would be approximately  $1 \times 10^{-22}$  which corresponds to only about a 1 per cent conversion of boron trichloride. Clearly the reaction of boron trichloride and hydrogen by purely thermal methods cannot lead to the

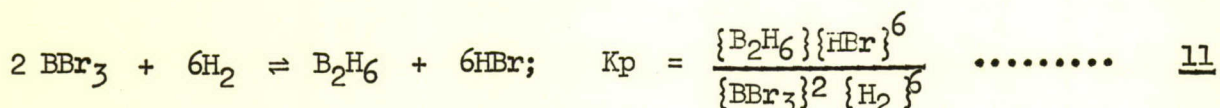
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relatively high conversions achieved in the electrical discharge. Probably the formation of highly active charged ions, which through lack of data cannot be dealt with thermodynamically, are responsible for the high conversion obtained, e.g.:

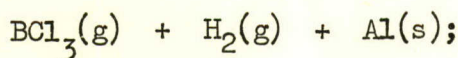


Similar arguments apply to the reaction of boron tribromide and hydrogen

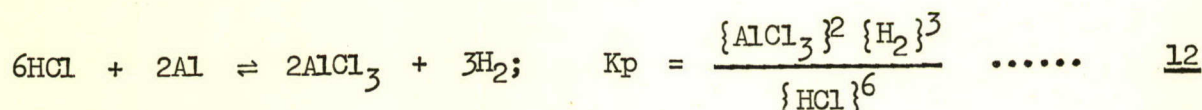
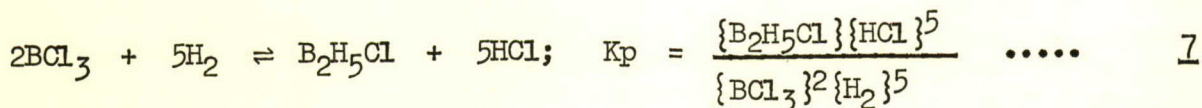
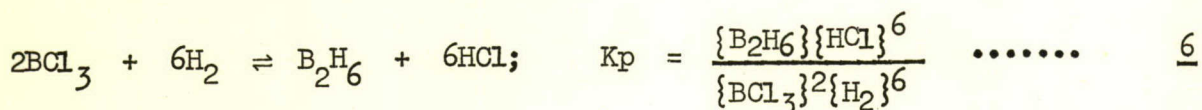


At present, no data are available for the equilibrium between monobromodiborane and diborane.

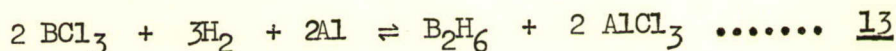
4.3 System 2



This system is represented by the three equations



The equilibrium constant for reaction 12 at 300°K is  $1 \times 10^{120}$  and the effect of aluminium on reactions 6 and 7 is to shift the equilibrium composition of the gases by continually removing hydrogen chloride as aluminium chloride. Thus the overall reaction



should go to completion. In practice, Hurd (11) found that, at 450°C, using a 6:1 ratio of hydrogen to boron trichloride, only a 30 per cent yield of diborane was obtained. It is probable that reactions 6 and 7 which lead to the formation of hydrogen chloride, are rate controlling.

/5. ....

5. THE PYROLYSIS OF DIBORANE

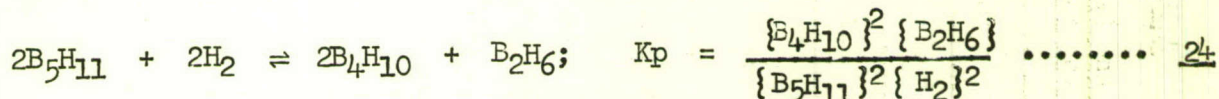
5.1 Introduction

The boron hydrides, other than diborane, are generally prepared by the pyrolysis of diborane. The free energies of the reactions which may be involved in pyrolysis experiments have been calculated and discussed by Bauer (5), and the present work has therefore been concerned with the calculation of the equilibrium constants for these reactions, and, in certain cases, the equilibrium position in the gas phase. The equilibrium constants for the reactions involving the principal hydrides are quoted in Table 3 (p. 8).

5.2 The Equilibria Between Diborane, Tetraborane and Dihydropentaborane

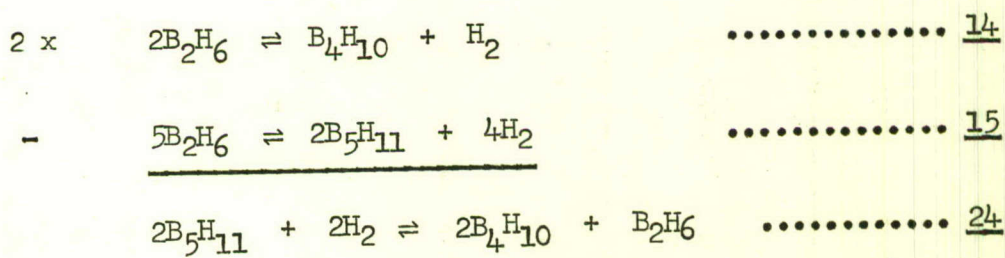
Bauer (5) has suggested that equilibria may be set up between diborane, tetraborane and dihydropentaborane, but he was unable to discuss the equilibria since the probable error in estimating the entropy values for the reactions was too great. In the present work it has proved possible to indicate which are the more probable values.

The reaction between dihydropentaborane and hydrogen to give diborane and tetraborane (reaction 24) was studied at 100°C by Stock and Mathing (13). Using a 20:1 ratio of hydrogen to dihydropentaborane, they obtained a 57.6 per cent conversion of dihydropentaborane to tetraborane and also found that very little side reaction occurred.



Now, it is a simple matter to calculate the equilibrium constant at a given percentage conversion, and Figure 1 is a graph of the logarithm of the equilibrium constant against percentage conversion of dihydropentaborane, assuming an initial 20:1 ratio of hydrogen to dihydropentaborane. It can be seen that a 57.6 per cent conversion corresponds to an equilibrium constant of  $2.8 \times 10^{-2}$ .

Reaction 24 can be obtained by a suitable combination of reactions 14 and 15 (Table 3), i.e.



/TABLE 3 .....

TABLE 3

Equilibrium Constants and Heats of Reaction for Reactions Involved in the Pyrolysis of Diborane

	Reactions	Equilibrium Constants at:				Heat of Reaction $\Delta H_{300}^{\circ}$ , kcal/mole
		Temperature, K				
		300°	400°	500°	600°	
14.	$2B_2H_6 \rightleftharpoons B_4H_{10} + H_2$ (a)	$1.85 \times 10^{-3}$	$1.16 \times 10^{-3}$	$8.71 \times 10^{-4}$	$7.16 \times 10^{-4}$	-1.16 <sup>#</sup>
15.	$5B_2H_6 \rightleftharpoons 2B_5H_{11} + 4H_2$ (a)	$6.10 \times 10^{-2}$	$3.54 \times 10^{-2}$	$2.67 \times 10^{-2}$	$2.21 \times 10^{-2}$	-4.65 <sup>#</sup>
16.	$5B_2H_6 \rightleftharpoons 2B_5H_9 + 6H_2$	$1.93 \times 10^{-1}$	$2.81 \times 10^{-2}$	$8.82 \times 10^{-2}$	$3.39 \times 10^{-3}$	-7.51
17.	$5B_4H_{10} \rightleftharpoons 4B_5H_9 + 7H_2$	$16.20$	$2.35$	$7.40 \times 10^{-1}$	$2.89 \times 10^{-1}$	-9.42 <sup>#</sup>
18.	$5B_4H_{10} \rightleftharpoons 4B_5H_9 + 7H_2$	$6.59 \times 10^{14}$	$4.41 \times 10^{13}$	$1.42 \times 10^{13}$	$9.72 \times 10^{12}$	-1.48 <sup>#</sup>
19.	$B_5H_{11} \rightleftharpoons B_5H_9 + H_2$	$1.89 \times 10^{43}$	$3.37 \times 10^{41}$	$3.01 \times 10^{40}$	$5.62 \times 10^{39}$	-10.57
20.	$5B_2H_6 \rightleftharpoons B_{10}H_{14} + 8H_2$	$6.04 \times 10^7$	$3.22 \times 10^7$	$2.21 \times 10^7$	$1.70 \times 10^7$	-3.06
21.	$5B_2H_6 \rightleftharpoons B_{10}H_{14} + 8H_2$	$2.97 \times 10^{20}$	$5.51 \times 10^{18}$	$1.08 \times 10^{18}$	$5.50 \times 10^{17}$	-15.5 <sup>#</sup>
22.	$2B_5H_9 \rightleftharpoons B_{10}H_{14} + 2H_2$	$4.50 \times 10^5$	$1.33 \times 10^5$	$7.56 \times 10^4$	$5.62 \times 10^4$	-6.0 <sup>#</sup>
23.	$5B_4H_{10} \rightleftharpoons 2B_{10}H_{14} + 11H_2$	$5.36 \times 10^{54}$	$7.72 \times 10^{51}$	$1.52 \times 10^{50}$	$1.18 \times 10^{49}$	-38.5 <sup>#</sup>
	$2B_5H_{11} \rightleftharpoons B_{10}H_{14} + 4H_2$	$9.60 \times 10^{20}$	$7.76 \times 10^{19}$	$1.71 \times 10^{19}$	$6.10 \times 10^{18}$	
	$6B_{10}H_{14} \rightleftharpoons 5B_{12}H_{12} + 12H_2$	$2.41 \times 10^{95}$	$2.44 \times 10^{88}$	$1.56 \times 10^{84}$	$2.35 \times 10^{81}$	

(a) Values uncertain due to the error in estimating the entropies. # Values quoted at 298°C

whence  $K_{p24} = (K_{p14})^2 / K_{p15}$ . An examination of the equilibrium constants for reactions 14 and 15 given in Table 3 shows that for  $K_{p24}$  to have a value of  $2.8 \times 10^{-2}$  at  $100^\circ\text{C}$ , the highest value of  $K_{p14}$  and the lowest value of  $K_{p15}$  must be used. Thus, the most probable values for the equilibrium constants of reactions 14 and 15 have been underlined in Table 3.

Figures 2 and 3 are similar to Figure 1, being graphs of the logarithm of the equilibrium constant against percentage conversion of diborane to tetraborane and to dihydropentaborane respectively. These graphs have been used to estimate the percentage conversion of initially pure diborane in equilibrium with (a) tetraborane, and (b) dihydropentaborane, at temperatures between  $300^\circ$  and  $600^\circ\text{K}$ . The results are given in Table 4.

TABLE 4  
Percentage Conversion of Diborane to (a) Tetraborane, and  
(b) Dihydropentaborane at Equilibrium

Temperature, $^\circ\text{K}$	% Diborane Converted to:	
	(a) Tetraborane	(b) Dihydropentaborane
300	33	59
400	27	50
500	24	45
600	21	40

For tetraborane, the yields vary between 33 and 21 per cent conversion of diborane as the temperature increases from  $300^\circ$  to  $600^\circ\text{K}$ . Similarly the corresponding yields for the dihydropentaborane reaction are 59 to 40 per cent. Since such high conversions of diborane to dihydropentaborane are rarely encountered in flow experiments it is unlikely that equilibrium is ever achieved with respect to this reaction. However, there may be instances where the rate of formation of dihydropentaborane is controlled by the equilibria, particularly in cases where the concentration of hydrogen is high, or when dihydropentaborane is being recirculated. Such practical conditions may occur during certain kinetic studies.

### 5.3 Reactions Leading to Pentaborane and Decaborane

Apart from nonvolatile solid, pentaborane and decaborane are the most thermodynamically stable of the boron hydrides. This is shown in Table 3, where it can be seen from the quoted equilibrium constants that diborane, tetraborane and dihydropentaborane all decompose completely to pentaborane, and pentaborane can decompose almost completely to decaborane. Even when an excess of eight moles of hydrogen per mole of decaborane formed is included

---

<sup>22</sup>The equilibrium constants for the respective reactions at  $100^\circ\text{C}$  are  $4.20 \times 10^{-2}$  and  $4.79 \times 10^{-2}$ . These values lead to an equilibrium constant for reaction 24 of  $3.6 \times 10^{-2}$ , in good agreement with the experimental value.

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in the products, as would occur if the pyrolysis of diborane went completely to decaborane, only 1 per cent pentaborane remains unconverted. In kinetic experiments therefore, the approach to the gaseous equilibrium can be entirely neglected.

In practice, most of the reactions in Table 3 are competing and the final products of pyrolysis can only be determined from kinetic considerations (14, 15).

5.4 Reactions Leading to Nonvolatile Solid

Bauer (5), assuming that the nonvolatile solid has a formula of  $B_{12}H_{12}$ , has shown that it is thermodynamically more stable than any of the volatile hydrides. All the volatile hydrides can therefore be converted to the nonvolatile solid, and as an illustration the equilibrium constants for the decomposition of decaborane (reaction 23, Table 3) are  $2.41 \times 10^{95}$  at  $300^\circ K$ , and  $2.35 \times 10^{81}$  at  $600^\circ K$ .

6. ALKYLATION REACTIONS

6.1 Introduction

Alkyl pentaboranes and alkyl decaboranes, while yielding rather less heat on combustion than the parent hydride, have more suitable physical properties for use as liquid fuels. Two methods of preparation are available:

- (a) By alkylation of the parent hydride (17, 18),
- (b) By reacting diborane in the presence of an olefine (16)

In order to investigate the thermodynamic aspects of reactions involving the alkyl derivatives, free energies of the compounds have been estimated by the method given in the Appendix (p. 14).

The equilibrium constants for a number of reactions involving ethyl pentaborane, ethyl decaborane and the diethyl derivatives have been calculated at  $300^\circ K$ , and the values quoted in Table 5. The relationship between temperature and equilibrium constant may be approximated to

$$\log K_p^T = \frac{300}{T} \log K_p^{300}$$

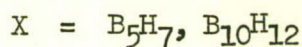
where  $K_p^T$  is the equilibrium constant at the absolute temperature of  $T^\circ$ .

/TABLE 5 .....

TABLE 5

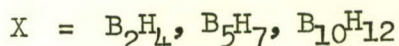
Equilibrium Constants and Heats of Reaction of Reactions  
Involving Ethylated Boron Hydrides

Reaction	Equilibrium Constant Kp at 300°K	Heat of Reaction ΔH <sub>300</sub> , kcal/mole
<u>25.</u> B <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub> ⇌ B <sub>2</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5</sub>	1 x 10 <sup>15</sup>	-31.1
<u>26.</u> B <sub>2</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub> ⇌ B <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1 x 10 <sup>15</sup>	-31.4
<u>27.</u> XH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> ⇌ XH·C <sub>2</sub> H <sub>5</sub>	1 x 10 <sup>15</sup> ± 3	-31
<u>28.</u> XH·C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub> ⇌ X(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1 x 10 <sup>15</sup> ± 5	-31
<u>29.</u> B <sub>2</sub> H <sub>6</sub> + 6C <sub>2</sub> H <sub>4</sub> ⇌ 2B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	4 x 10 <sup>80</sup>	-158.5
<u>30.</u> 5B <sub>2</sub> H <sub>6</sub> + 2B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ⇌ 6B <sub>2</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5</sub>	4 x 10 <sup>13</sup>	-28.1

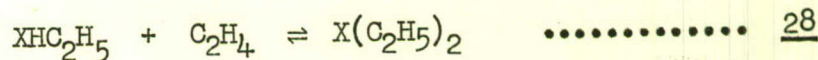


6.2 Alkylation of the Parent Hydride

The ethylation of a boron hydride with ethylene is indicated in Table 5 by reaction 27, which represents equally well a straight reaction and any corresponding catalysed reactions. (17, 18):



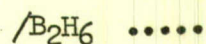
Reaction 28 represents the formulation of the diethyl derivative:



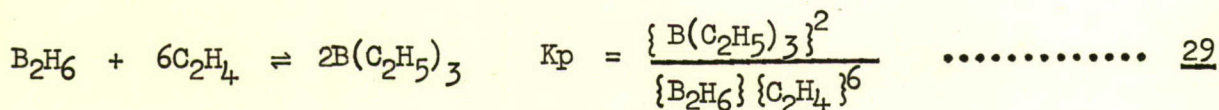
Consequent on the empirical method of calculating the free energies, these reactions all have an equilibrium constant of approximately 10<sup>15</sup>, which indicates the greater thermodynamic stability of the alkyl boron hydrides over the parent hydrides. These reactions are all exothermic to the extent of 31 kcal/mole.

6.3 Pyrolysis of Diborane in the presence of an Olefine (e.g., Ethylene)

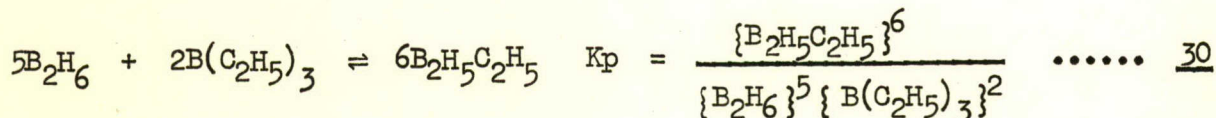
When diborane and ethylene are heated together a number of reactions may occur, several of which have been reported in the literature. If an excess of ethylene is used at a reaction temperature of 100°C, the main product is triethyl boron (19).



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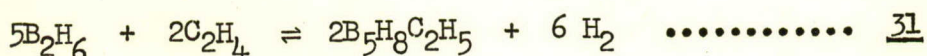


This reaction has an equilibrium constant of  $4 \times 10^{80}$ . It is also well known (7) that triethyl boron will react with diborane to give a series of ethylated diboranes, e.g:



The equilibrium constant for the reaction is large,  $4 \times 10^{13}$ , again indicating the theoretical completeness of the reaction to monoethyldiborane. These two reactions, 29 and 30, may be combined to give the reaction of diborane with ethylene to form monoethyldiborane, which, as indicated in Section 6.2, has an equilibrium constant of  $1 \times 10^{15}$ .

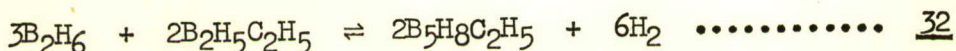
At temperatures of around  $100^\circ\text{C}$ , therefore, ethylene reacts with diborane to give both triethyl boron and monoethyldiborane. At the higher temperatures at which diborane is converted to pentaborane, it can be seen that there are a number of possible ways for the alkylation reactions to occur. If one assumes that at these temperatures ethylene reacts with diborane to form monoethylpentaborane, without the formation of intermediates,



the equilibrium constant would be  $10^{30}$  greater than that for the straight pyrolysis of diborane :



However, if it is assumed that monoethyl diborane is a stable intermediate, the equilibrium constant for the reaction



will be the same as that for reaction 16. Similarly, triethyl boron may be used as the alkylating agent. Theoretically, there is therefore no reason why diborane and ethylene, diborane and triethyl boron and diborane and monoethyl diborane should not give a high yield of ethyl pentaborane, when heated together. Obviously as in the other reactions examined, kinetic considerations will be of great importance in determining the actual result.

/Whilst .....

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Whilst only the formation of ethyl pentaborane has been dealt with in this section, similar arguments apply to the formation of the decaborane derivatives. However, it has been reported (20) that attempts to prepare methyl pentaborane by the pyrolysis of diborane and trimethyl boron led to yields of 7 per cent; the poor yield must be due to kinetic factors.

7. BIBLIOGRAPHY

1. A.P. Altshuller, N.A.C.A. Research Memo. E55926, 1955.
2. A.J. Owen, Unpublished Data.
3. W.H. Evans, D.D. Wagman and E.J. Prosen, Nat. Bur. of Stand. Rept. No. 4943, 1956.
4. F.D. Rossini, "Tables of Selected Values of Chemical Thermodynamic Constants", Bureau of Standards, Washington, 1948.
5. S.H. Bauer, J. Amer. Chem. Soc., 1958, 80, 294.
6. W.H. Schechter, C.B. Jackson, R.M. Adams, "Boron Hydrides and Related Compounds", Callery Chemical Company, May, 1954.
7. A. Stock, "Hydrides of Boron and Silica", Oxford Univ. Press, 1933.
8. H.I. Schlesinger and A.B. Burg, J. Amer. Chem. Soc., 1931, 53, 4321.
9. A. Stock and W. Sutterlin, Ber., 1934, 67, 407.
10. D.T. Hurd, B.P., 623,760; 623,761:U.S.P. 2,596,690.
11. D.T. Hurd, J. Amer. Chem. Soc., 1949, 71, 20; G.E.C. Rept. No. 55203, 1947.
12. A. Stock, H. Martine and W. Sutterlin, Ber., 1934, 67, 396.
13. A. Stock and W. Mathing, Ber., 1936, 69, 1456.
14. L.V. McCarty and P.A. DiGiorgio, J. Amer. Chem. Soc., 1951, 73, 3138.
15. J.K. Bragg, L.V. McCarty and F.J. Norton, J. Amer. Chem. Soc., 1951, 73, 2134.
16. R.J. Heaston, quoted by R.A. Carpenter, A.R.S. Journal, 1959, 29, 8.
17. R.W. Blundell, N.G.T.E. Report No. NT. 345.
18. I. Dunstan and J.V. Griffiths, E.R.D.E. Report No. 17/R/59.
19. D.T. Hurd, J. Amer. Chem. Soc., 1948, 70, 2053.
20. J.H. Lamneck and S. Kaye, N.A.C.A. Report E58 E12.
21. L. Pauling, "Nature of the Chemical Bond", Cornell Univ. Press, 1940.
22. R.L. Williams, Private communication.

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APPENDIX

Estimation of the Free Energies of Some Alkyl Boron Hydrides

Thermodynamic data is available only for the more common boron hydrides and the ethyl derivatives of diborane. Interest in the ethyl derivatives of pentaborane and decaborane necessitated the estimation of their free energies.

The free energy of formation of a compound from its elements in their standard states  $\Delta F$ , is represented by the expression:

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

where  $\Delta H$  is the heat of formation,  $\Delta S$  the entropy of formation and  $T$  the absolute temperature. The heat of formation can be readily calculated by the standard empirical method (21), while the entropy values have been estimated by a comparison of the boron hydrides with the carbon analogues. This method of comparison is justified for the following reasons.

- (i) The entropies of a homologous hydrocarbon series show a constant increase of 10 entropy units per  $\text{CH}_2$  group. This is shown clearly in Table 6 for the series starting with ethane, ethylene, benzene and naphthalene.
- (ii) The entropies of methyl diborane and ethyl diborane are 11.4 and 20.6 entropy units greater than the entropy of diborane, i.e. and increase of approximately 10 to 11 entropy units per  $\text{CH}_2$  group.
- (iii) The boiling point and melting point difference between the alkyl boron hydrides and the parent hydride are closely paralleled by the corresponding hydrocarbons (see Table 7), and these physical properties are related to the entropy values.
- (iv) The vibrational spectra of the boron-carbon bonds in alkyl boron hydrides occur at the same wavelength as the spectra of carbon-carbon bonds (22), and this property of the molecule is again related by partition functions to the entropy value.

The hydrocarbon series chosen for the comparison are the series starting with ethane and ethylene for diborane, benzene for pentaborane, and naphthalene for decaborane. Entropies of the alkyl boron hydrides have been estimated by an addition of 10 entropy units per  $\text{CH}_2$  group to the parent hydride. Values of the heat of formation, entropy and free energy of formation at  $300^\circ\text{C}$  of the alkyl boron hydrides are given in Table 8, (p. 16).

/TABLE 6 .....

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TABLE 6

The Entropies of Hydrocarbons, Boron Hydrides and  
their Alkyl Derivatives

Compound	Entropy, cal/deg. C.mole		
	Parent	Methyl Derivative	Ethyl Derivative
Diborane, B <sub>2</sub> H <sub>6</sub>	55.34	66.7	75.9
Ethane, C <sub>2</sub> H <sub>6</sub>	54.85	64.51	74.12
Ethylene, C <sub>2</sub> H <sub>4</sub>	52.45	63.8	73.04
Pentaborane, B <sub>5</sub> H <sub>9</sub>	65.95	-	-
Benzene, C <sub>6</sub> H <sub>6</sub>	64.34	76.42	86.15
Decaborane, B <sub>10</sub> H <sub>14</sub>	85.09	-	-
Naphthalene, C <sub>10</sub> H <sub>8</sub>	80.43	(1) 90.21	99.94
		(2) 90.83	100.56

TABLE 7

The Melting Points and Boiling Points of Hydrocarbons,  
Boron Hydrides and their Alkyl Derivatives

Compound	Melting Points and Boiling Points, °C					
	Parent		Methyl Derivative		Ethyl Derivative	
	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
Diborane	-165.5	-92.5				
Ethane	-172	-88.3	-189.9	-42.17	-135	0
Ethylene	-169.4	-103.9	-185	-47.0	-130	-5
Pentaborane	-46.6	58			-85	104
Benzene	5.51	80	-95	110	-94	136
Decaborane	99.6	213	-12	223	-25	218
Naphthalene (1)	80	218	-22	240	-14	258
			(2)	35	245	-19

/TABLE 8 .....

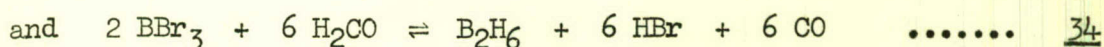
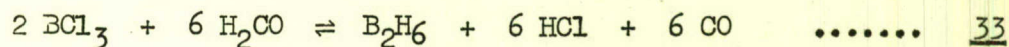
TABLE 8

The Heats of Formation, Free Energy and Entropy of  
Boron Hydrides and their Alkyl Derivatives

Compound	Thermodynamic Function		
	Heat of Formation, $\Delta H_{300}^{\circ}$ , kcal/mole	Free Energy of Formation, $\Delta F_{300}^{\circ}$ , kcal/mole	Entropy, $S^{\circ}$ , cal/deg.C.mole
Diborane	7.53	19.78	55.34
Methyl diborane	-8.5	10.1	66.7
Ethyl diborane	-11.1	14.5	75.9
Diethyl diborane	-30	9	93
Pentaborane	15.02	39.32	65.95
Methyl pentaborane	-1 ± 3	30 ± 4	75 ± 1
Ethyl pentaborane	-3.5 ± 3	34 ± 4	85 ± 1
Diethyl pentaborane	-22.5 ± 5	29 ± 7	105 ± 2
Decaborane	27	71	85.09
Methyl decaborane	11 ± 2	61 ± 3	95 ± 1
Ethyl decaborane	8.5 ± 4	66 ± 4	105 ± 1
Diethyl decaborane	-10.5 ± 4	60 ± 5	125 ± 3

NOTE ADDED IN PROOF

Section 4 of this report shows that in order to obtain high conversions of a boron trihalide to diborane, an active form of hydrogen must be used. A novel method of obtaining this active hydrogen has been patented by O. Glemser, German Patent 945, 943, in which boron tribromide and formaldehyde react on an activated copper on keiselguhr catalyst at 380° to 420°C to give a 70 per cent yield of diborane. Free energy changes for the reactions



have been calculated at 300°, 500° and 700°K and the values obtained tabulated below:

TABLE 9

Free Energy Changes and Heats of Reaction

Reaction No.	Free Energy Changes, kcal/mole at:			Heat of Reaction kcal/mole
	300°K	500°K	700°K	
<u>33</u>	+36.4	-0.2	-28.4	+61.8
<u>34</u>	+21.0	-15.6	-43.6	+770

The negative free energy changes for both reactions in the temperature range 500° to 700°K indicate the thermodynamic feasibility of the processes. The low cost of formaldehyde and the high yield of diborane of 70 per cent make the processes appear attractive and, while the reactions are highly endothermic, the reaction temperature can be maintained by burning the carbon monoxide in the product gases after the removal of the other more valuable products.

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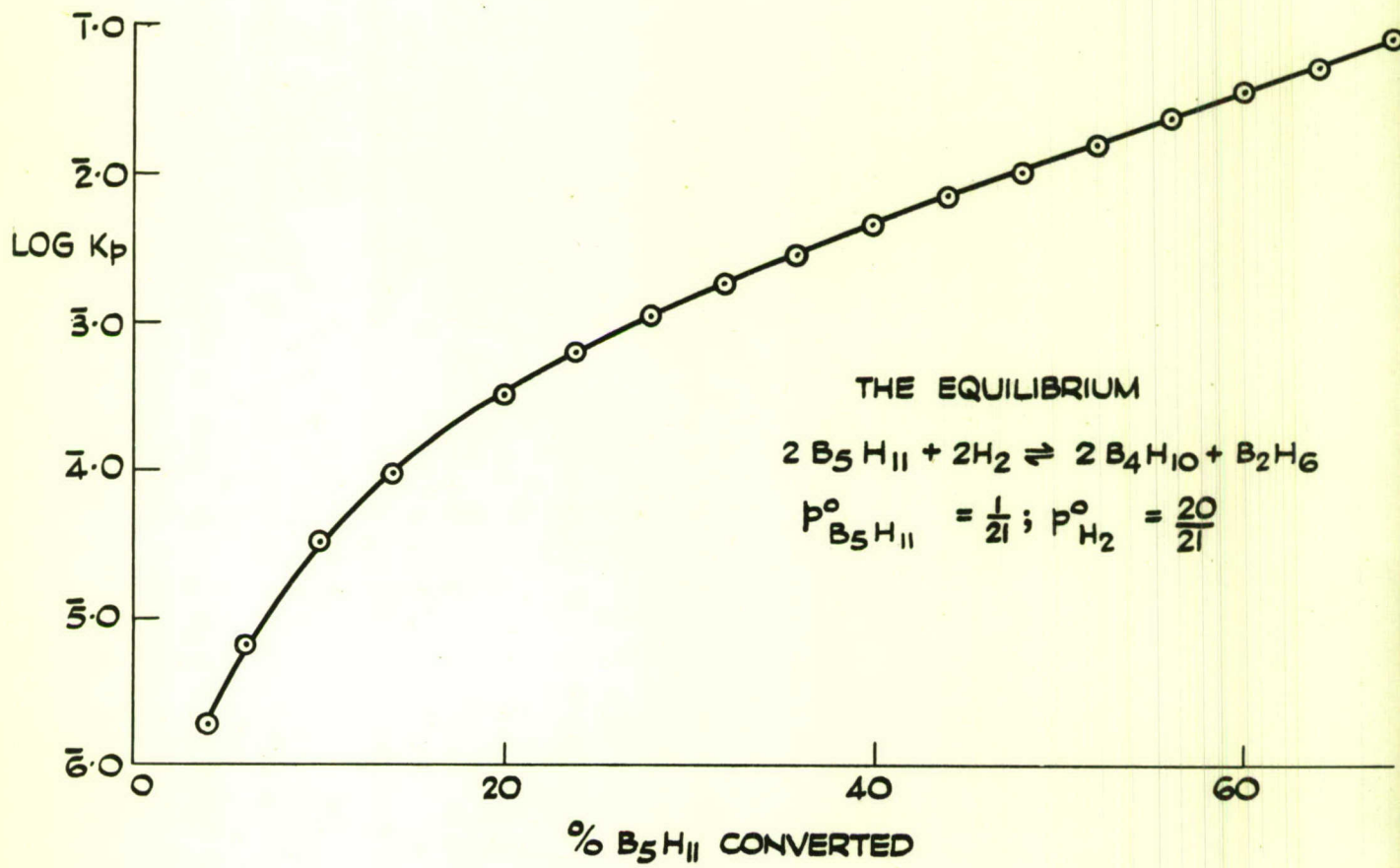


FIG. 1.

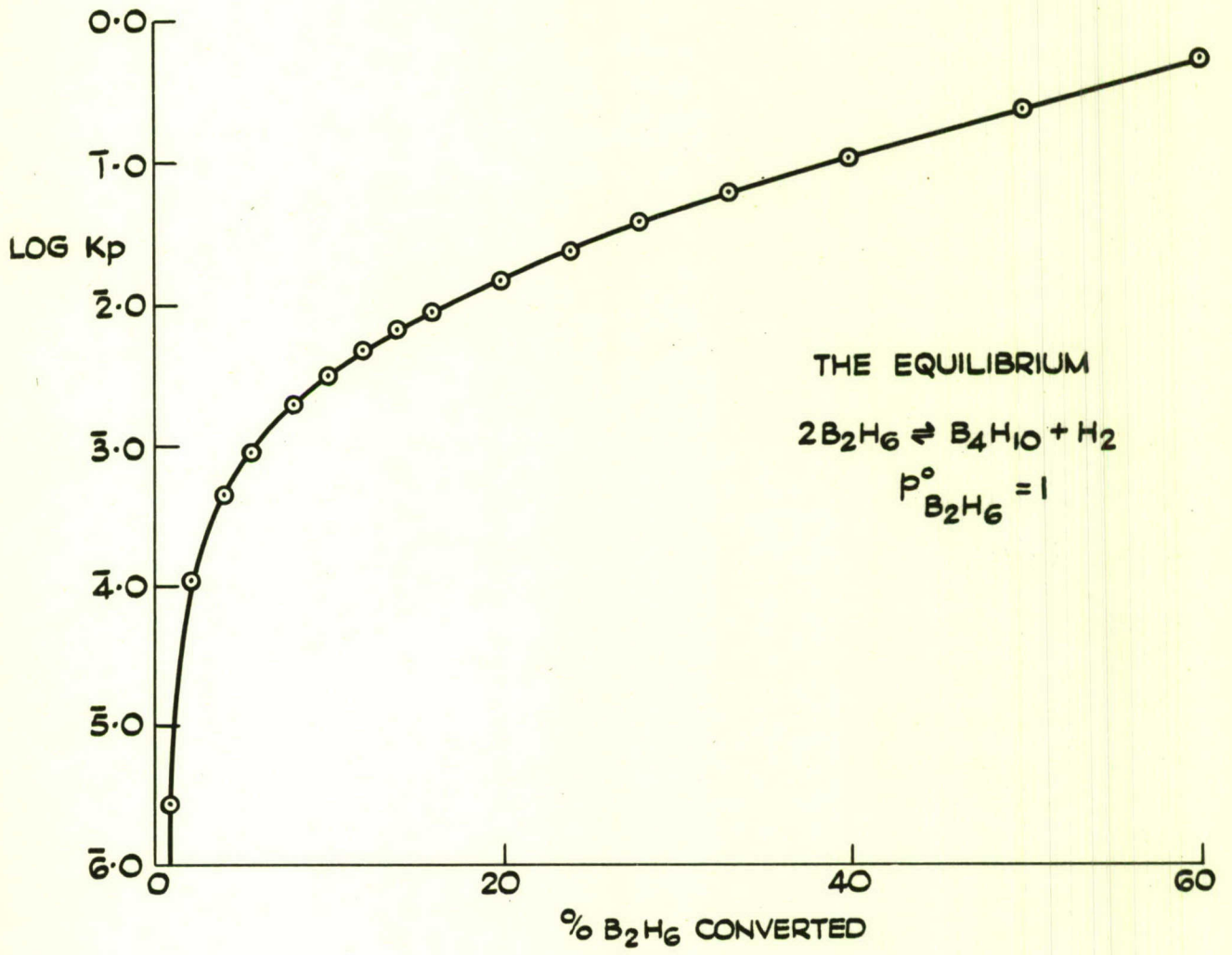


FIG. 2.

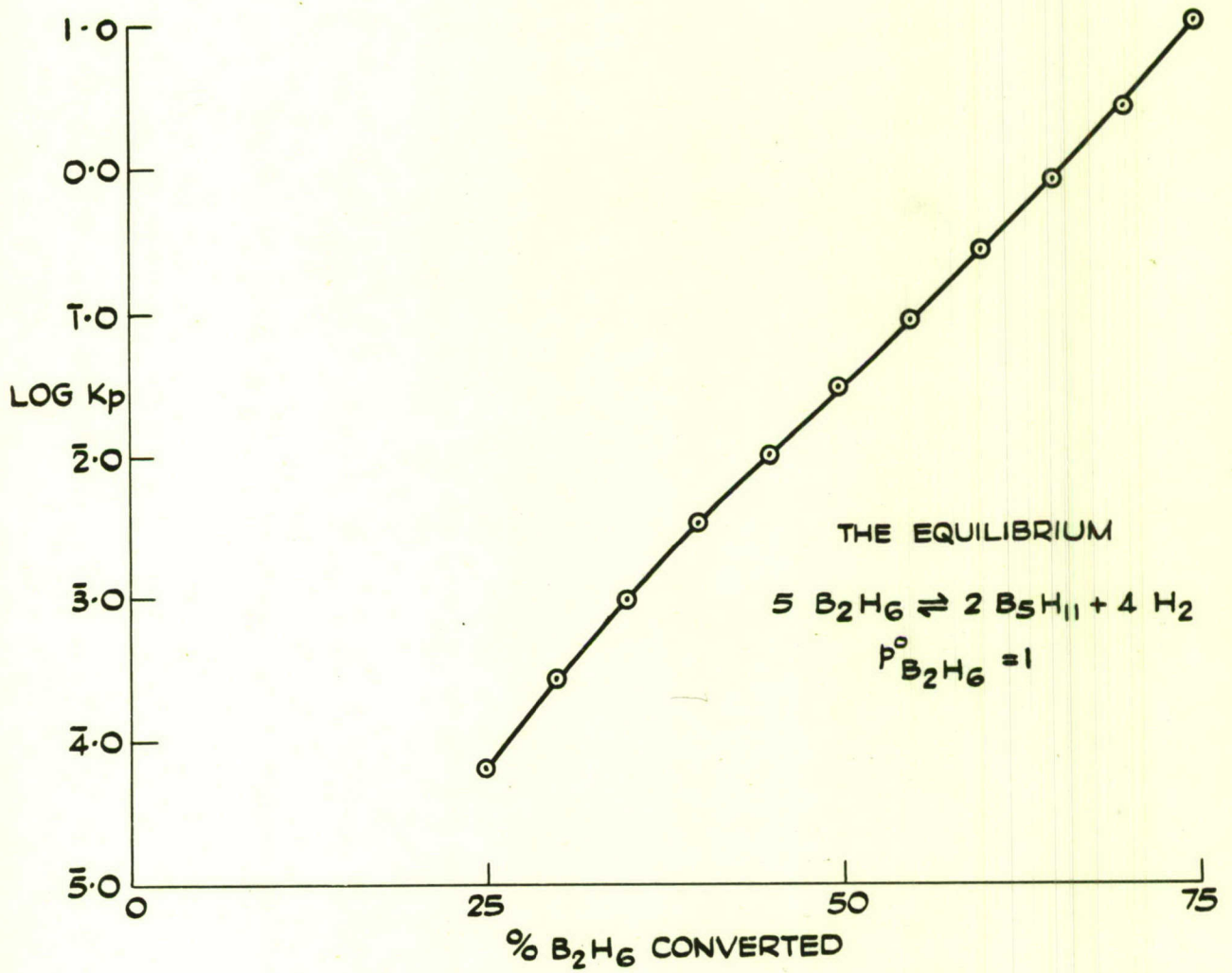


FIG. 3.



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