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HUGHES TOOL COMPANY · AIRCRAFT DIVISION
Culver City, California



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INFRARED SPECTRA AND THERMODYNAMIC PROPERTIES
OF TRIFLUOROBOROXINE, (FBO)₃
FINAL

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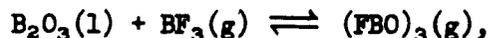


SUMMARY

Infrared spectra of isotopically-normal and B¹⁰-enriched trifluoroboroxines were taken of samples prepared by the high-temperature (500°C) reaction of isotopically labeled boron trifluoride and silica followed by quenching the product at -150°C. Trifluoroboroxine disproportionates above -135°C to boron trifluoride and boric oxide. Spectra of the labeled trifluoroboroxines and their resulting boric oxides are presented.

By use of "argon windows" in a high-temperature infrared cell the B-O-F system was examined at various temperatures up to 1200°C; the presence of monomer FBO could not be detected either by absorption or by emission.

From direct measurements of the equilibrium constant of the reaction



the heat and entropy of reactions were determined as a function of temperature over the range 700° to 1000°K. Combined with literature values for boric oxide and boron trifluoride, the heat of formation of (FBO)₃, ΔH_f° at 298°K, is -567.8 kcal/mole, and the entropy value, S° , at this temperature is 81.0 cal/°/mole. The temperature functions of $\bar{\ln} K_p$, ΔH_f , and ΔS_f are given.

Analysis of data derived from transpiration experiments indicates that the agreement of values for ΔH_f° is fortuitous, but the experimental errors manifest themselves in the entropy term. The change in the heat of formation of (FBO)₃ with temperature has been found to be greater than anticipated by the Dow (JANAF) thermodynamic tables for B₃O₃F₃.



INTRODUCTION

The need for accurate heats of formation data on the B-O-F system is readily apparent to all workers in the fields of solid and liquid propellants. A number of contractors have been engaged in determining such data, and their findings to date are summarized below:

Aeronutronic (1) arrived at a value of $\Delta H_f^{\circ} 298 (\text{FBO})_3 = -570 \pm$ kcal/mole by a transpiration study of the reaction $\text{B}_2\text{O}_3(\text{gl}) + \text{BF}_3(\text{g})$.

Rocket Power, Inc. (2) obtained a value of $\Delta H_f^{\circ} 298 (\text{FBO})_3 = -567.8 \pm 0.5$ kcal/mole also by a transpiration study of the same reaction.

Esso R and E (3) gives an approximate value of $\Delta H_f^{\circ} 298 (\text{FBO})_3 = -570$ kcal/mole based on a study of the heats of solution of $(\text{FBO})_3$ in water and in methanol.

Ohio State Univ. (4) obtained an approximate value of $\Delta H_f^{\circ} 298 \text{FBO} = -144$ kcal/mole by mass spectral analysis.

Arthur D. Little, Inc. (5) arrived at a value of $\Delta H_f^{\circ} 298 \text{FBO} = -130 \pm 20$ kcal/mole also by mass spectral analysis.

A cursory inspection of the data gives the impression that the reported heats of formation check well; however, this agreement is fortuitous because the heat of reaction of $\text{BF}_3 + \text{B}_2\text{O}_3 \rightarrow (\text{FBO})_3$ is very small in comparison to the heats of formation of BF_3 and B_2O_3 .

An evaluation of the two transpiration studies reveals serious discrepancies which do not appear in the final result. The transpiration technique makes use of a flow of BF_3 gas over a weighed sample of B_2O_3 , and the loss in weight of B_2O_3 as a function of temperature is taken as a measure of the amount of $(\text{FBO})_3$ formed. In the Aeronutronic study the apparatus was made of metalware,



whereas in the Rocket Power Inc. study, quartz beads were placed on both the inlet and outlet sides of the furnace. "The incoming gas (BF_3) was heated to the experimental temperature by its passage over a bed of quartz beads thereby insuring a constant reaction temperature" (2). In this connection attention is called to the reaction of BF_3 with SiO_2 to form $(\text{FBO})_3$ and SiF_4 (6). Actually the reaction of BF_3 with SiO_2 has been found to be faster than with B_2O_3 ; consequently, data for obtaining equilibrium constants between BF_3 and $(\text{FBO})_3$ have no meaning when the experiments are carried out in the presence of silica (quartz). As a further complication, the SiF_4 can react with B_2O_3 to regenerate BF_3 (7), with the possible formation of a silicon oxyfluoride.

In the case of the study of the heats of solution of $(\text{FBO})_3$, the material was claimed to be badly contaminated (as evidenced by reported physical properties); consequently, any data derived from these experiments must be regarded as very preliminary.

Obviously, the free-saving feature of all these experiments is the low heat of reaction of $\text{BF}_3 + \text{B}_2\text{O}_3 \rightarrow (\text{FBO})_3$. Thus, although the value of the heat of formation of $(\text{FBO})_3$ centers about -570 kcal/mole, the entropy values derived by the various contractors differ considerably from each other.

CURRENT EFFORT

In an effort to check the heat of formation of $(\text{FBO})_3$ and FBO by a more direct method, as well as obtain some spectroscopic data on this compound, this Contractor conducted a 5 man-months study on the B-O-F system, which is reported here. The spectroscopic data are reported first since certain techniques, developed here, are used in the kinetic-equilibrium studies. While these data



obtained here are considered preliminary, the techniques employed can be improved to yield precise values.

Spectroscopic Studies

Recent advances by this Contractor in both low- and high-temperature infrared spectroscopy permit the study of the B-O-F system over a wide range of temperatures. Prior to the undertaking of the present study, this Contractor studied the infrared spectra of both isotopically normal and B¹⁰-enriched trifluoroboroxine, obtained by a low-temperature technique. Because of the importance of this work to the present study, the details of the spectra and data are included here.

This Contractor also developed a new technique of using "argon windows" so that it is now possible to obtain infrared absorption spectra at temperatures above 1000°C — previous work at these temperatures was limited to emission spectra.

Low Temperature Study

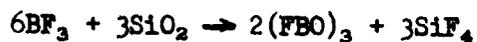
The reaction of boron trifluoride with various oxygen-containing compounds leads to the formation of a compound with the empirical formula of (BOF)_x. Ruff and co-workers (8) envisioned a coordination complex between BF₃ and B₂O₃; however, Baumgarten and Bruns (9) and Goubeau and Keller (10) have presented experimental evidence for the formation of trifluoroboroxine. In subsequent work with Raman spectra Goubeau and Keller (11) demonstrated the existence of the cyclic B-O ring (B₃O₃X₃). This ring structure was verified by mass spectral studies of trimethylboroxine (12).

In the present low-temperature studies the boron trifluoride (either isotopically normal--80% B¹¹-- or B¹⁰-enriched--96% B¹⁰) was purified by complexing



with acetyl chloride followed by fractionation through a -155°C bath prior to each experiment. No impurities could be detected by infrared analysis. The infrared cell, shown both in detail and assembled in Fig. 1, is similar in design to that described by Becker and Pimentel (13). The inner plate holder assembly is offset in the cell so that both the condensed phase and gas phase can be examined by a mere shift in cell position in the spectrometer. The copper block and sodium chloride plate were maintained at the desired temperature by means of precooled nitrogen.

Boron trifluoride of known isotopic content was passed over quartz heated to 500°C , where the following reaction occurred:



The gas stream then was cooled rapidly on the NaCl plate, which was maintained at -150°C . At this temperature the trifluoroboroxine condensed on the NaCl window, while the unreacted boron trifluoride and silicon tetrafluoride were removed by pumping. The samples were cooled to -196°C , and their spectra were recorded on a Beckman IR-4 infrared spectrophotometer equipped with NaCl optics.

Goubeau and Keller (10) reported that trifluoroboroxine is stable only above 250°C ; it is possible, however, to isolate and maintain this compound at temperatures below -135°C , at which temperature the rate of disproportionation becomes negligible. When trifluoroboroxine is allowed to warm to temperatures above -135°C , it disproportionates rapidly into boron trifluoride and boric oxide in a 1:1 ratio, as indicated by chemical analysis. The course of the disproportionation was followed by alternately warming the sample in the infrared cell to predetermined temperatures and quenching in liquid nitrogen, pumping off the evolved boron trifluoride, and examining the spectra of the residue. The disproportionation proceeds through isolatable unstable intermediates and is



Figure 1. Low-Temperature Infrared Cell

essentially complete (>99 percent) within one hour at room temperature.

Boron trifluoride reacts much faster with silica than with boric oxide. When B^{10} -enriched boron trifluoride was passed rapidly through a heated quartz tube coated with isotopically-normal boric oxide and the resulting trifluoroboroxine was subsequently decomposed, the evolved BF_3 had the same isotopic content as the initial BF_3 , thus indicating no reaction with B_2O_3 . However, with longer contact time, B^{11} -enrichment in the product BF_3 showed that some reaction with B_2O_3 had occurred.

The infrared spectra of both isotopically-normal and B^{10} -enriched trifluoroboroxines together with their respective boric oxides are shown in Fig. 2. The infrared frequencies of the trifluoroboroxines and their assignments as compared with mesitylene and trimethylboroxine are given in Table I.

Planar trifluoroboroxine belongs to symmetry point group (14) D_{3h} . The 14 internal vibrations are of the following species with the indicated Raman and infrared activity (14): $3A_1'(R) + 2A_2'$ (inactive) + $2A_2''(I) + 5E'(RI) + 2E''(R)$. From analogy with mesitylene (1,3,5-trimethylbenzene) (15), one would expect only four vibrations to have infrared bands in the sodium chloride range (above 650 cm^{-1}). By no coincidence, four principal bands have been observed and are assigned as shown in Table I. These observed bands differ from those postulated for thermodynamic calculations (16).

Of special interest is the band at 966 cm^{-1} , which is assigned to the doubly degenerate out-of-phase stretching mode of the three B-F groups. Its small B^{10} -isotope shift of ca 2 cm^{-1} confirms the ring structure. Any other reasonable structure would exhibit a much larger isotope effect. For example, the minimum shift for an F-B-O monomer is 8 cm^{-1} [calculated by treating the molecule as diatomic F-(BO)]. Further, the predicted frequency for the B-F

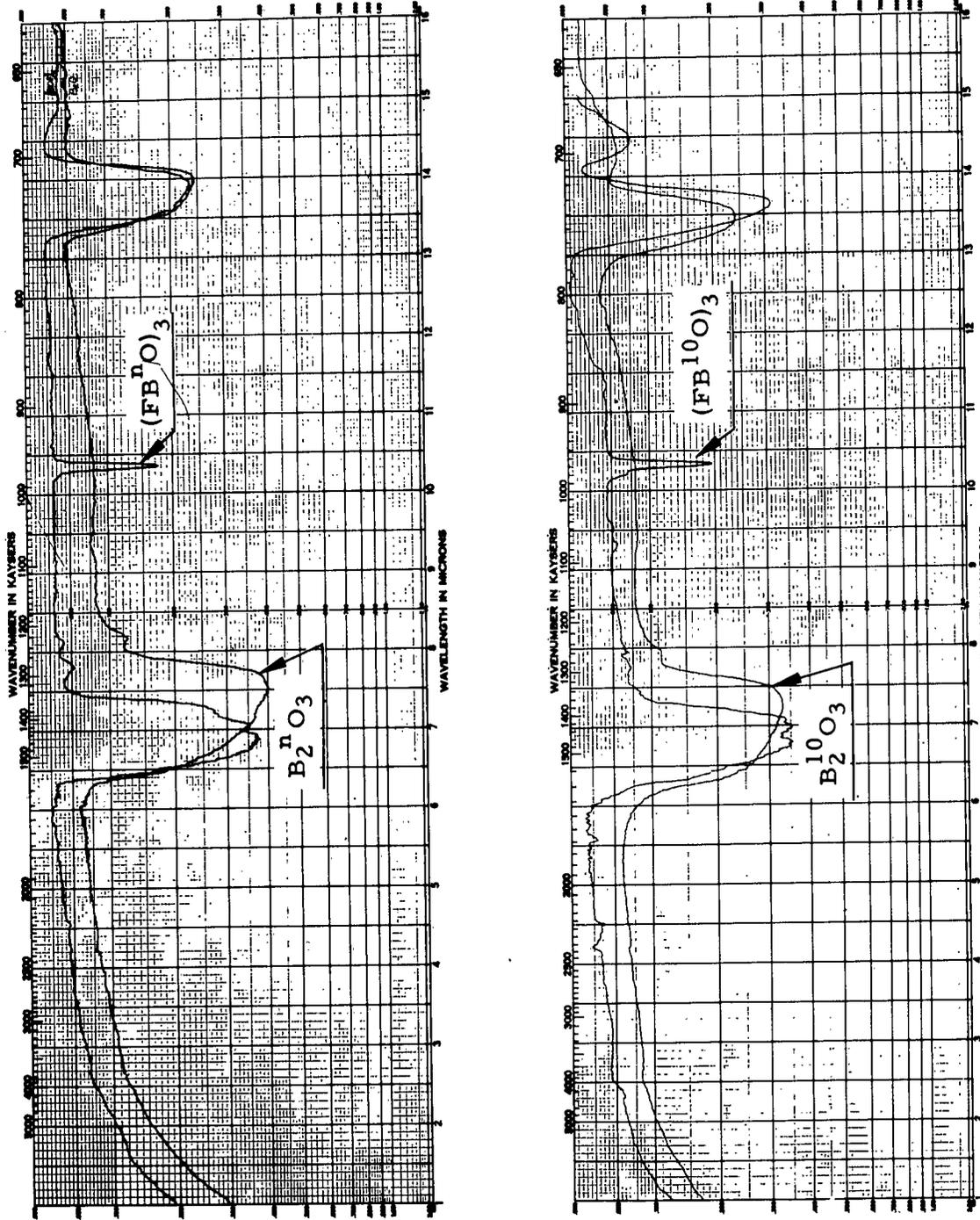


Figure 2. Infrared Spectra of Labeled Trifluoroboroxines and Labeled Boric Oxides



TABLE I

Infrared spectra of trifluoroboroxine
and assignments compared with mesitylene and trimethylboroxine (cm^{-1})

Assignment for $\text{F}_3\text{B}_3\text{O}_3$	$\text{F}_3\text{B}_3^{11}\text{O}_3^a$	$\text{F}_3\text{B}_3^{10}\text{O}_3$	Mesitylene	$\text{Me}_3\text{B}_3^{11}\text{O}_3$	$\text{Me}_3\text{B}_3^{10}\text{O}_3$
ring puckering (out of plane, a_2'')	714 s ^b	733	ν_4 690	784	786
B-F stretching (out of phase, e')	966 m ^c	968	ν_{20} 930	918	932
ring stretching (e')	1381 s ^b	1431	ν_{19} 1385	1227	1260
ring stretching (e')	1450 s ^b	1477	ν_8 1610	1384	1430
(unassigned)	1233 w	1260	- -	-	-
(unassigned)	1280 w	1290	- -	-	-

^a s = strong, m = medium, w = weak

^b broad

^c sharp



single-bond is ca 1096 cm^{-1} ; nothing is observed in that vicinity.

High-Temperature Studies

The high-temperature infrared cell used in the present study was designed for temperatures up to ca 1200°C . The heater surrounding the chamber was a double tungsten wire-wound unit operating in a hydrogen atmosphere. The temperature of the cell was thermocouple-controlled. A flow of argon gas over the ends of the cell proved to be effective in preventing undesirable gases from entering the cell, and thus acted as "windows". Hence it was possible to use this cell for obtaining IR absorption spectra as well as emission spectra.

A series of infrared absorption spectra of pure boron trifluoride at temperatures up to the limit of 1200°C showed essentially no change from a spectrum run at room temperature. No emission spectrum of boron trifluoride could be detected under similar temperature conditions.

Boric oxide (B_2O_3) at temperatures up to 1000°C did not give any emission spectrum; however, at higher temperatures (1350°C) the emission spectrum has been reported in the literature (17).

To study the B-O-F system by absorption spectroscopy, a stream of boron trifluoride gas was passed into a side chamber containing magnesium oxide, and then the products were passed into the main chamber. No absorption spectrum could be obtained under these conditions; obviously the boron trifluoride reacted completely with the magnesium oxide, otherwise the BF_3 absorption spectrum would have been observed.

In the case of the emission spectroscopic study of the B-O-F system, a mixture of magnesium fluoride and boric oxide was heated directly in the main

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chamber. The observed emission spectra as a function of temperature over the wave length regions of 6-8 μ and 14-15 μ are shown in Figure 2a. The emission bands are attributed to the $(\text{FBO})_3$ species, and agree fairly well with the absorption bands of $(\text{FBO})_3$ given in Figure 2. The slight shift from 714 cm^{-1} for the solid to ca 700 cm^{-1} for the gas phase is due to the change in state and is expected [compare, for example, with the shift for liquid boric oxide to the vapor phase (17)]. The reported corresponding emission bands for B_2O_3 at 1350°C are 1302 cm^{-1} and 756 cm^{-1} so there is no question that the observed bands do not belong to B_2O_3 . Unfortunately, the emission spectrum in the region of 966 cm^{-1} (B-F absorption stretching frequency) could not be obtained due to intense absorption in this region caused by an impurity in the optical system of the instrument.

The conclusion is made that no FBO monomer is present in any detectable amounts in the infrared spectra at temperatures up to 1100°C.



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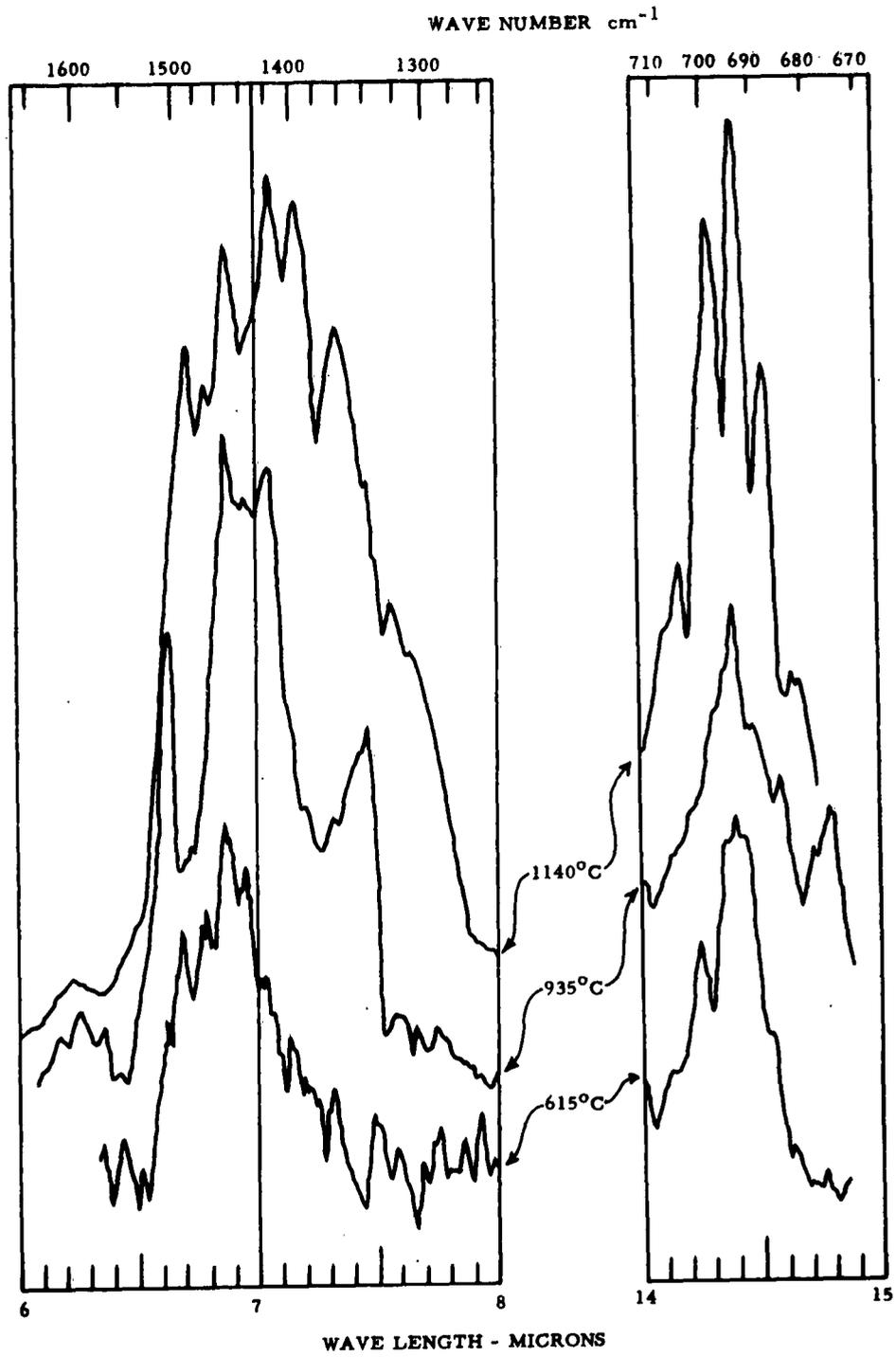


Figure 2a. Effect of Temperature on the Infrared Emission Spectrum of Trifluoroboroxine (Over the range 6-8 μ and 14-15 μ)



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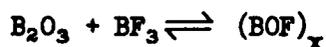
Kinetic-Equilibrium Studies

The most convenient, and probably most accurate, method for determining the heats of formation (ΔH_f^0) of $(\text{FBO})_3$ and FBO is that derived from a study of the reaction of boron trifluoride and boric oxide. The heats of formation of these two reactants are known with some precision, and from the heat of reaction (ΔH_r) one can obtain the heat of formation of $(\text{FBO})_3$. To obtain the heat of reaction, one must measure the equilibrium constant, $K_p = \frac{n(\text{FBO})_3}{n\text{BF}_3}$, where n = mole fraction of species, as a function of temperature. If only the trimer is present as the product, the over-all reaction is independent of pressure. Upon dissociation of the trimer to the monomer, the reaction becomes pressure dependent. From the Clausius-Clapeyron equation the heat of reaction is related to the equilibrium constant, viz.,

$$\frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = - \frac{\Delta H_r}{R}$$

Determination of Equilibrium Constant

All sources of error inherent to a flow system can be eliminated by determining the equilibrium composition of the reaction,



under static conditions. For such experiments the following procedure was used: A known amount of boron trifluoride with an excess amount of boric oxide was charged into an evacuated stainless steel bomb and heated to the desired temperature until equilibrium had been established. The equilibrium then is frozen by releasing and rapidly cooling the mixture gases to -196°C . The free boron trifluoride is removed at a temperature below -135° [the $(\text{FBO})_3$ does not disproportionate below this temperature] and measured. The $(\text{FBO})_3$ then is warmed to



room temperature and the amount of boron trifluoride formed by the disproportionation measured. The amount of residual boric oxide is determined by standard chemical methods. The equilibrium constant at each temperature is given directly by the ratio of the amount of $(\text{FBO})_3$ and the amount of BF_3 . Excellent agreement had been found between the amounts of BF_3 and B_2O_3 resulting from the disproportionation of $(\text{FBO})_3$.

In addition to determining the ratio of $(\text{FBO})_3$ and BF_3 , the equipment was designed so as to detect any change in total pressure of the system, thus serving as a measure of the amount of dissociation of the trimer to monomer. At temperatures up to the limit of the apparatus (1100°K) no change in pressure could be detected, thus indicating no monomer formation. The apparatus could have detected as little as 0.5 percent monomer.

Table II summarizes the data for the equilibrium constant.

Thermodynamic Functions

Equilibrium Constant: For purpose of comparison, the equilibrium constant (logarithm function) derived by the various contractors is plotted against the reciprocal of the absolute temperature in Fig. 3. The present work indicates that the plot has a slight curvature rather than a straight line -- in contrast to data obtained by other workers. The wide disparity in the curves indicates a serious discrepancy. Data obtained by Aeronutronics are in the same general area of the current work. Since these data (1) have been obtained by an extrapolation method which is subject to certain variations, the general agreement of data is considered good. It has already been pointed out that the data obtained by Rocket Power (2) must be considered unacceptable because the presence of silica in the reactor will upset the equilibrium of $(\text{FBO})_3$ and BF_3 .

TABLE II

Equilibrium constant and free energy of reaction for the system
 $B_2O_3(l) + BF_3(g) = (BFO)_3(g)$ as a function of temperature

$T^{\circ}K$	$\frac{1}{T^{\circ}K} \times 10^3$	P total mm.Hg	K_p	$-\ln K_p$	ΔF $-RT \ln K_p$ cal./mole
678	1.476	256	0.189	1.666	2244.4
811	1.233	348	.288	1.245	2006.3
811	1.233	494	.321	1.136	1830.6
811	1.233	484	.274	1.295	2086.8
834	1.200	671	.292	1.231	2040.0
928	1.077	633	.473	0.749	1381.1
984	1.016	622	.460	0.777	1519.2
1030	0.971	573	.667	0.405	828.9



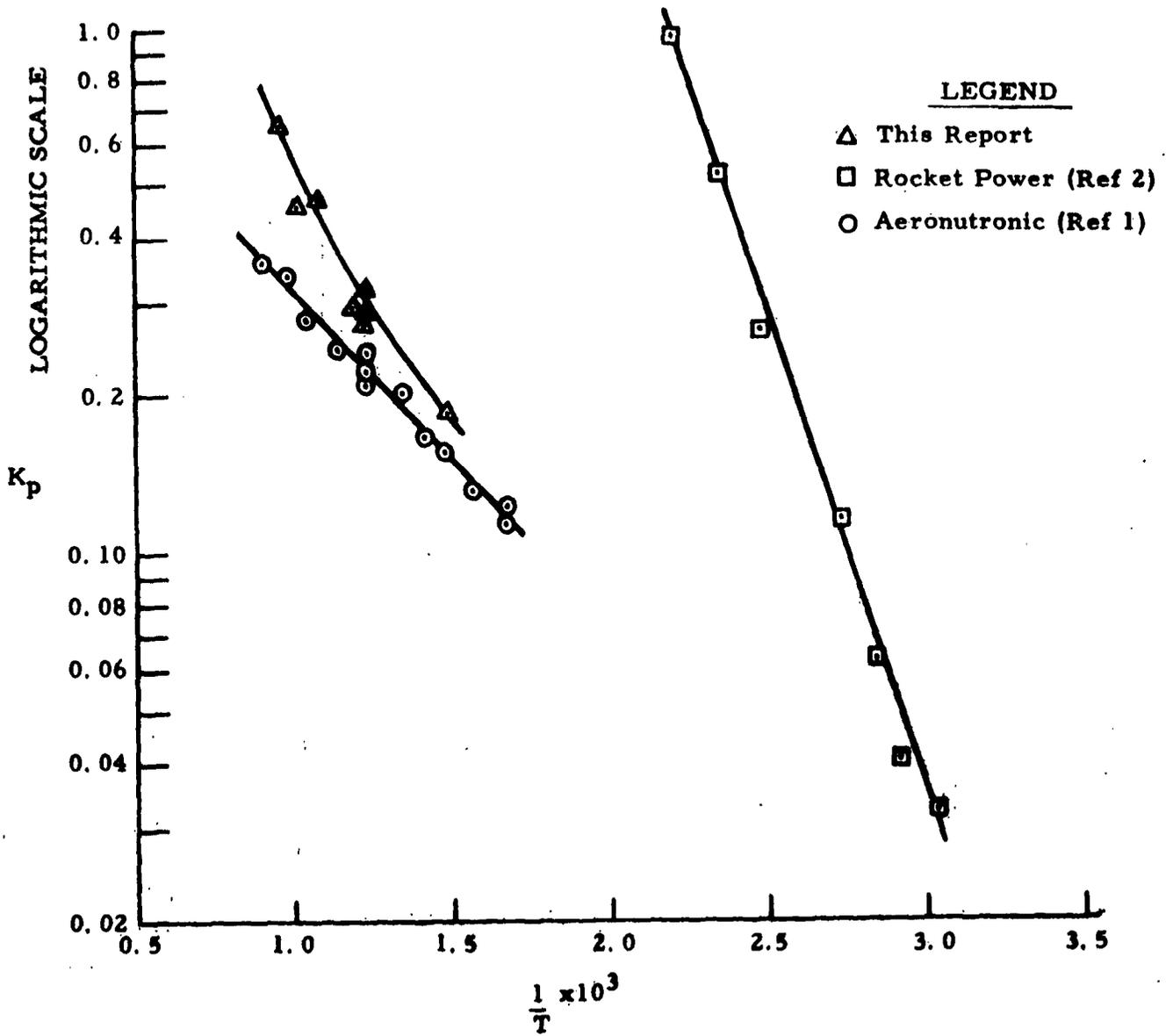


Figure 3. Equilibrium Constant as a Function of Temperature



The curve given in Fig. 3 can be represented by the following equation:

$$\ln K_p = 0.716 - 742/T - 0.489 \ln T + 2.70 \times 10^{-3} T + 0.126 \times 10^{-6} T^2$$

over the temperature range of 700 to 1000°K.

Heat of Reaction: The heat of reaction can be obtained from the slope of the curve in Fig. 3 and can be represented by the equation

$$\Delta H_r \text{ kcal/mole} = 1.476 - 0.972 \times 10^{-3} T + 5.367 \times 10^{-6} T^2 + 0.501 \times 10^{-9} T^3$$

over the temperature range of 700° to 1000°K.

Entropy of Reaction: Fig. 4 gives the change in free energy, ΔF , of the system as a function of temperature as determined by the various contractors. The wide disparity of the curves again points to serious errors in results. In contrast to the value of the heat of formation of $(FBO)_3$ which is relatively insensitive to the heat of reaction, ΔH_r , the entropy value, S° , is sensitive to the entropy of reaction. Even small errors in the entropy term become very serious at high temperatures, hence the need for accurate data.

The entropy of reaction is related to the free energy and heat of reaction, viz.,

$$\Delta S_r = \frac{\Delta H_r}{T} - \frac{\Delta F_r}{T} = \frac{\Delta H_r}{T} + R \ln K_p$$

and can be expressed by

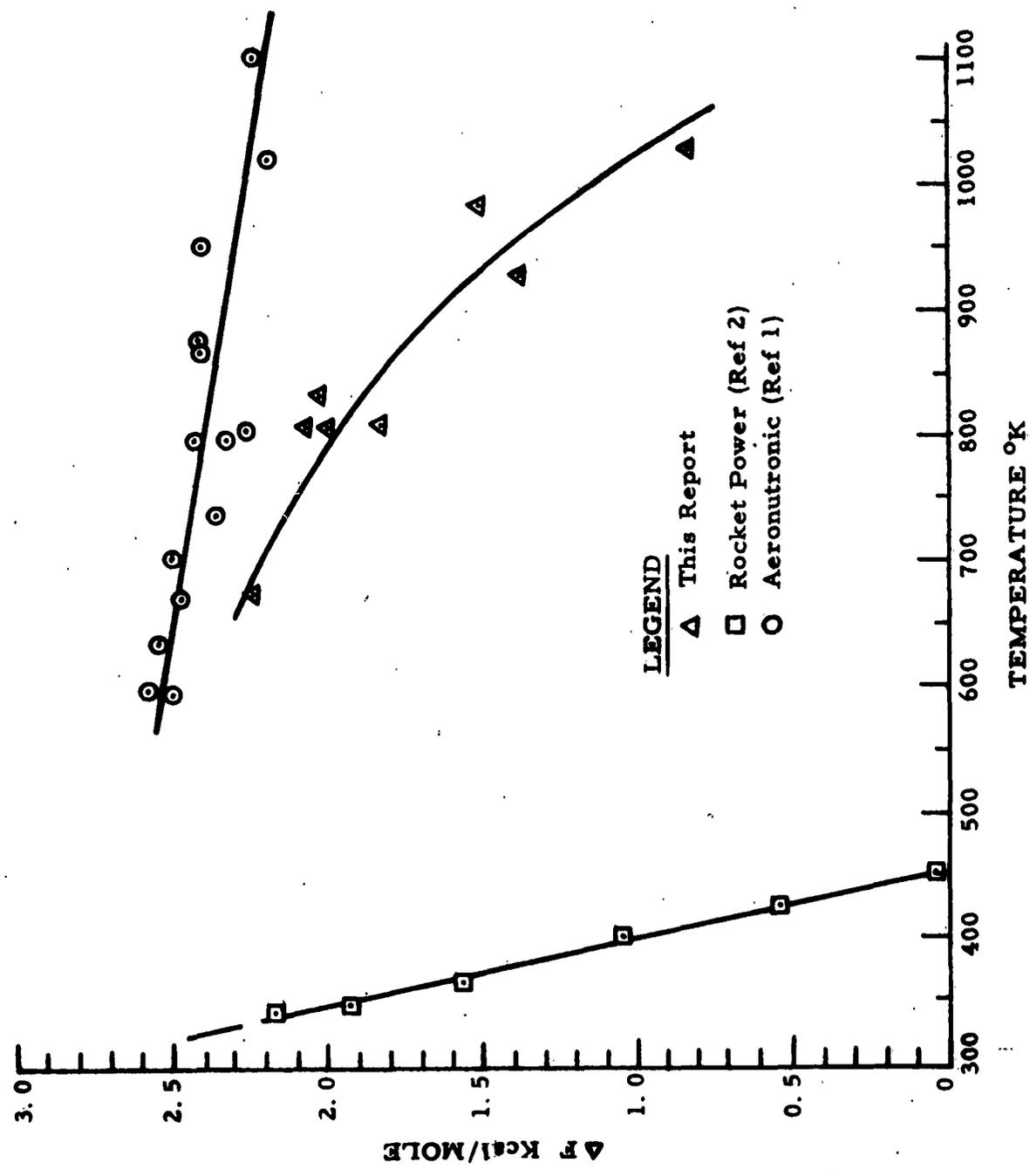
$$\Delta S_r \text{ cal/°/mole} = 0.450 - 0.972 \ln T + 10.733 \times 10^{-3} T + 0.752 \times 10^{-6} T^2$$

over the temperature range of 700° to 1000°K.

Heat of Formation: The heat of formation of $(FBO)_3$ is calculated from the heats of formation of the reactants (16) and heat of reaction, all values



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- Rocket Power (Ref 2)
- Aeronutronic (Ref 1)

Figure 4. Change in Free Energy as a Function of Temperature

being taken at the same temperature.

$$\Delta H_f^\circ(\text{FBO})_3 = \Delta H_f^\circ \text{B}_2\text{O}_3 + \Delta H_f^\circ \text{BF}_3 + \Delta H_r$$

$$\text{At } 1000^\circ\text{K}, \Delta H_f^\circ(\text{FBO})_3 = -296.95 - 271.11 + 6.40 = -561.7 \text{ kcal/mole}$$

$$\text{At } 298^\circ\text{K}, \Delta H_f^\circ(\text{FBO})_3 = -305.34 - 270.00 + 7.60^* = -567.8 \text{ kcal/mole}$$

 * ΔH_r is corrected for the heat of fusion of boric oxide (5.91 kcal/mole) at temperatures below the melting point of boric oxide (723°K)

A comparison of the heat of formation of $(\text{FBO})_3$ over the temperature range of 300° to 1000°K as calculated by the data obtained here and as listed by the Dow JANAF table (16) is given in Fig. 5. The difference in the two curves is regarded as significant for thermodynamic calculation.

Entropy: The entropy of $(\text{FBO})_3$ is calculated in an analogous manner to the heat of formation, viz.,

$$S^\circ(\text{FBO})_3 = S^\circ \text{B}_2\text{O}_3 + S^\circ \text{BF}_3 - \Delta S_r$$

$$\text{At } 1000^\circ\text{K}, S^\circ(\text{FBO})_3 = 48.99 + 79.32 - 5.22 = 123.1 \text{ cal/}^\circ\text{/mole}$$

At 298°K, the value of $S^\circ(\text{FBO})_3$ is estimated at 81.0 cal/°/mole after taking into account the entropy of fusion of boric oxide.

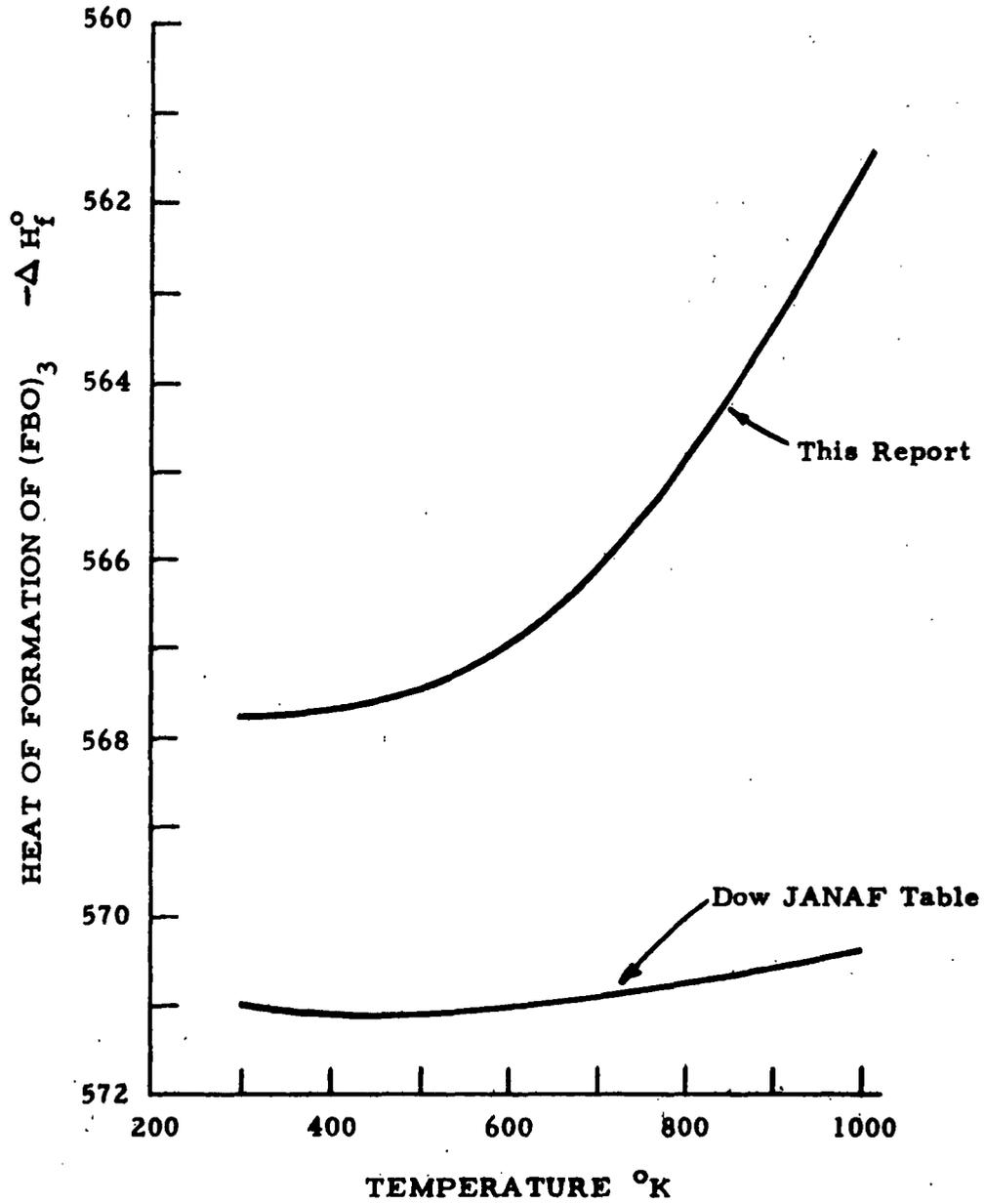


Figure 5. Change in Heat of Formation of (FBO)₃ with Temperature



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