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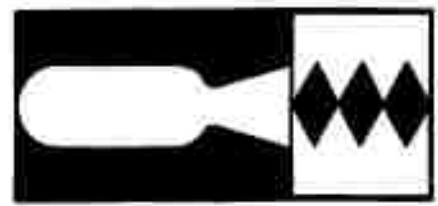
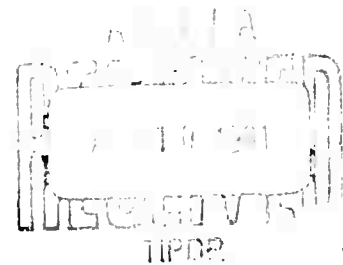
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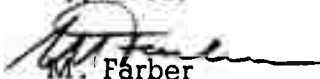
THERMODYNAMICS OF REACTIONS
INVOLVING LIGHT METAL OXIDES
AND PROPELLANT GASES

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ABSTRACT

Employing a new experimental technique, Molecular Flow Reaction Studies, a heat of formation, H_{f298K} of -142 ± 3 kcal/mole is reported for the molecule $BOF(g)$.

The reaction $B_2O_3(l) + BF_3(g) = (BOF)_3(g)$ was employed for this study. Earlier transpiration studies yielded values for H_{f298K} of -567.8 ± 0.5 kcal/mole and S_{298K} of 89.9 ± 2 cal/ $^{\circ}$ /mole for the trimer $BOF_3(g)$.

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THERMODYNAMICS OF REACTIONS INVOLVING LIGHT METAL OXIDES AND PROPELLANT GASES

I. INTRODUCTION

It has been observed that the experimental performance of high energy propellants falls well short of the calculated theoretical performance, particularly in those propellants containing light metals such as aluminum or boron. This discrepancy in performance may very well be due to incorrect thermodynamic assumptions for the theoretical calculations, leading to excessively high predicted theoretical performance.

Such errors could be eliminated, with a resultant saving in time and testing, if more accurate thermodynamic information were available in certain areas. It is the purpose of this program to study the high temperature formation of oxyhalogens of aluminum and boron, such as BOF, $(\text{BOF})_3$, BOCl , AlOF , and AlOCl . There is particular current interest in the gaseous BOF molecule. The formation of these compounds at high temperatures is a definite possibility when B_2O_3 and Al_2O_3 are in contact with the gaseous halogens or halide compounds (1 - 5). The formation of such compounds as exhaust products would influence the performance of the light metal solid propellants considerably. Hence, it is felt desirable to study the formation of these compounds and to measure their thermodynamic properties. It is also anticipated that similar reactions with beryllium oxide might occur and may be investigated after completion of the boron and aluminum studies.

A value for the heat of formation and entropy of the trimer $(\text{BOF})_3$ has been determined by the transpiration method and reported in the preceding Quarterly Reports (6 and 7). The work reported included a transpiration study of crystalline and liquid B_2O_3 with BF_3 in the temperature range of 300 to 1000°K. Employing the latest available heats of formation from the National Bureau of Standards (7), the heat of reaction yielded a value of -567.8 kcal/mole for H_{f298K} and 89.9 cal per degree per mole for S_{298K} for $(\text{BOF})_3(g)$. At a total pressure of one atmosphere the trimer $(\text{BOF})_3$ is

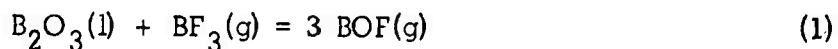
virtually stable with a negligible amount of dissociation occurring to the monomer.

Partial pressure measurements utilizing BF_3 and argon mixtures have indicated no change in the equilibrium of the thermodynamic constants of the system in the temperature range studied. Evidence obtained from these experiments shows that no appreciable amount of the monomer BOF(g) exists at a reaction pressure of one atmosphere. A study of surface area effects of glassy and crystalline boric oxide was made to determine their effect on the thermodynamic equilibrium.

During the preceding report period a new experimental technique, Molecular Flow Reaction Studies, was developed for determining the thermodynamic data of the monomer. Essentially, this method involves an impinging gas at the temperature of the reaction, striking the reacting material at pressures allowing free molecular flow. Since the accommodation coefficient for temperature is therefore unity, the molecular concentration of new molecules is determined by the equilibrium constant. A total of some twenty experiments employing the molecular flow reaction method in a temperature range of 1000 to 1250°K were undertaken. A heat of formation, H_{f298K} of $-142 \pm 3\text{kcal/mole}$ is reported for the monomer BOF(g) .

II. THERMODYNAMICS OF THE MONOMER BOF

A detailed discussion, both theoretical and experimental, of a new technique, Molecular Flow Reaction Studies, was reported in the preceding Quarterly Report (7). Therefore, the report for this period will concern itself with a discussion of some twenty experimental determinations for the reaction



The investigation was made in the temperature range from 1000 to 1250°K and at pressures of 10^{-5} atmospheres. The pressure for each determination

was measured directly over the reaction zone. The experimental data are tabulated in Table I and include the temperature, flow rate of BF_3 , pressure of gas in the reaction zone, and the amount of B_2O_3 reacting. The equilibrium constant

$$K_p = \frac{P^3(\text{BOF})}{P(\text{BF}_3)} \quad (2)$$

and the free energy

$$\Delta F = -RT \ln K_p \quad (3)$$

are calculated for each determination and are shown in Table II. Employing the JANAF Thermodynamic Tables (8) for entropies of $\text{B}_2\text{O}_3(\text{l})$, $\text{BF}_3(\text{g})$ and $\text{BOF}(\text{g})$, values were calculated for the ΔH of reaction from the second law of thermodynamics

$$\Delta F = \Delta H - T \Delta S \quad (4)$$

at each temperature and are tabulated in Column 5 of Table II.

In order to obtain a value for the heat of formation of BOF at the experimental temperature, heats of formation of the reactants $\text{B}_2\text{O}_3(\text{l})$ and $\text{BF}_3(\text{g})$ were obtained from the JANAF tables (8).

The $H_f(\text{BOF})(\text{g})$ at the experimental temperature is calculated as follows:

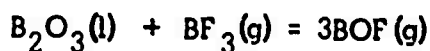
$$H(\text{BOF})(\text{g}) = \frac{\Delta H_r + H(\text{B}_2\text{O}_3)(\text{l}) + H(\text{BF}_3)(\text{g})}{3} \quad (5)$$

where H is the heat of formation and enthalpy of the molecule at the given temperature.

The value for $H_{298\text{K}}$ of BOF is calculated from the heat content of $\text{BOF}(\text{g})$ as given in the JANAF tables (8).

TABLE I

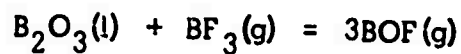
EXPERIMENTAL DATA FOR MOLECULAR FLOW REACTION STUDY OF EQUILIBRIUM



Run No.	Temp. °K	Pressure BF ₃ (atm)	Weight Loss B ₂ O ₃ moles/hr.	Flow of BF ₃ Moles/hr. ³
103	1000	4.35×10^{-5}	1.87×10^{-5}	6.25×10^{-4}
104	1000	1.48×10^{-5}	2.4×10^{-6}	1.2×10^{-4}
105	1100	1.48×10^{-5}	3.02×10^{-5}	1.2×10^{-4}
106	1100	1.48×10^{-5}	2.3×10^{-5}	1.2×10^{-4}
107	1200	9.87×10^{-6}	6.62×10^{-5}	1.2×10^{-4}
108	1200	1.52×10^{-5}	6.62×10^{-5}	1.2×10^{-4}
109	1200	1.30×10^{-5}	9.82×10^{-5}	1.3×10^{-4}
110	1007	1.58×10^{-5}	7.2×10^{-6}	3.75×10^{-4}
111	1148	1.97×10^{-5}	1.07×10^{-5}	3.89×10^{-5}
112	1054	1.84×10^{-5}	2.17×10^{-5}	3.89×10^{-4}
113	1150	1.84×10^{-5}	9.15×10^{-5}	3.35×10^{-4}
114	1098	1.91×10^{-5}	3.81×10^{-5}	4.02×10^{-4}
115	1203	1.91×10^{-5}	1.29×10^{-4}	3.35×10^{-4}
116	1075	1.86×10^{-5}	2.70×10^{-5}	3.93×10^{-4}
117	1174	1.86×10^{-5}	9.18×10^{-5}	3.75×10^{-4}
118	1151	1.84×10^{-5}	6.97×10^{-5}	4.02×10^{-4}
119	1253	2.07×10^{-5}	1.85×10^{-4}	3.95×10^{-4}
120	1252	1.91×10^{-5}	1.91×10^{-4}	3.19×10^{-4}
121	999	1.78×10^{-5}	1.65×10^{-5}	4.13×10^{-4}

TABLE II

THERMODYNAMIC PROPERTIES FOR THE EQUILIBRIUM



Run No.	Temp °K	K _p	ΔF kcal	ΔH _r kcal	BOF (g) -H _f 298K kcal
103	1000	7.63 × 10 ⁻¹³	55.4	133	145
104	1000	2.64 × 10 ⁻¹⁴	62.0	140	142
105	1100	2.24 × 10 ⁻¹¹	53.5	138	143
106	1100	1.77 × 10 ⁻¹¹	54.0	139	145
107	1200	1.67 × 10 ⁻¹⁰	53.5	145	140
108	1200	3.98 × 10 ⁻¹⁰	51.5	143	141
109	1200	1.13 × 10 ⁻⁹	49.0	141	142
110	1007	2.66 × 10 ⁻¹⁴	62.3	141	142
111	1148	2.75 × 10 ⁻¹¹	55.1	143	141
112	1054	2.36 × 10 ⁻¹²	55.5	137	143
113	1150	8.2 × 10 ⁻¹¹	52.7	141	142
114	1098	3.94 × 10 ⁻¹²	56.9	141	141
115	1203	2.08 × 10 ⁻¹²	53.0	145	140
116	1075	1.48 × 10 ⁻¹²	57.7	141	142
117	1174	5.18 × 10 ⁻¹¹	55.0	145	140
118	1151	2.04 × 10 ⁻¹¹	56.1	144	140
119	1253	4.39 × 10 ⁻¹⁰	53.2	148	139
120	1252	8.3 × 10 ⁻¹⁰	51.8	147	140
121	999	2.77 × 10 ⁻¹³	57.0	135	144

$$H_{f298K}(\text{BOF})(g) = H(\text{BOF})(g) - (H - H_{298})(\text{BOF})(g) \quad (6)$$

All experimental results gave an average value for $H_{f298K}(\text{BOF})(g)$ of -142 ± 3 kcal/mole. The experimental points are plotted in Figure 1.

In order to show that $(\text{BOF})_3$ is nearly completely dissociated to the monomer, calculations reported in the Third Quarterly Report (7) were repeated employing the data reported above. For the reaction



the equilibrium constant is given as

$$K = \frac{27 x^3 p^2}{(n + 2x)^2 (n - x)} \quad (8)$$

where x = moles of $(\text{BOF})_3$ dissociating
 $n - x$ = moles of $(\text{BOF})_3$ undissociated
 $3x$ = moles of BOF formed
 p = reaction pressure

For a reaction study value of 1200°K the value for K in equation (8) is 1.7×10^{-8} and shows that $(\text{BOF})_3$ is nearly completely dissociated to the monomer. These calculations are taken from the JANAF Tables (8) which report a theoretical entropy S_{298K} of 78.4 cal/o/mole which is somewhat lower than the experimental value of 89.9 cal/o/mole reported in the Second Quarterly Report (6). Randall (9), at the University of Wisconsin, has calculated a value in excess of 85 e.u. for the entropy of $(\text{BOF})_3(g)$ at 298°K . He also reports a value of -567.5 kcal/mole from a theoretical calculation of H_{f298K} of $(\text{BOF})_3(g)$. Further qualitative evidence that $(\text{BOF})_3$ does not appear in any quantity at these pressures and temperatures is lack of formation of $\text{B}_2\text{O}_3(s)$ in the cold zone of the apparatus.

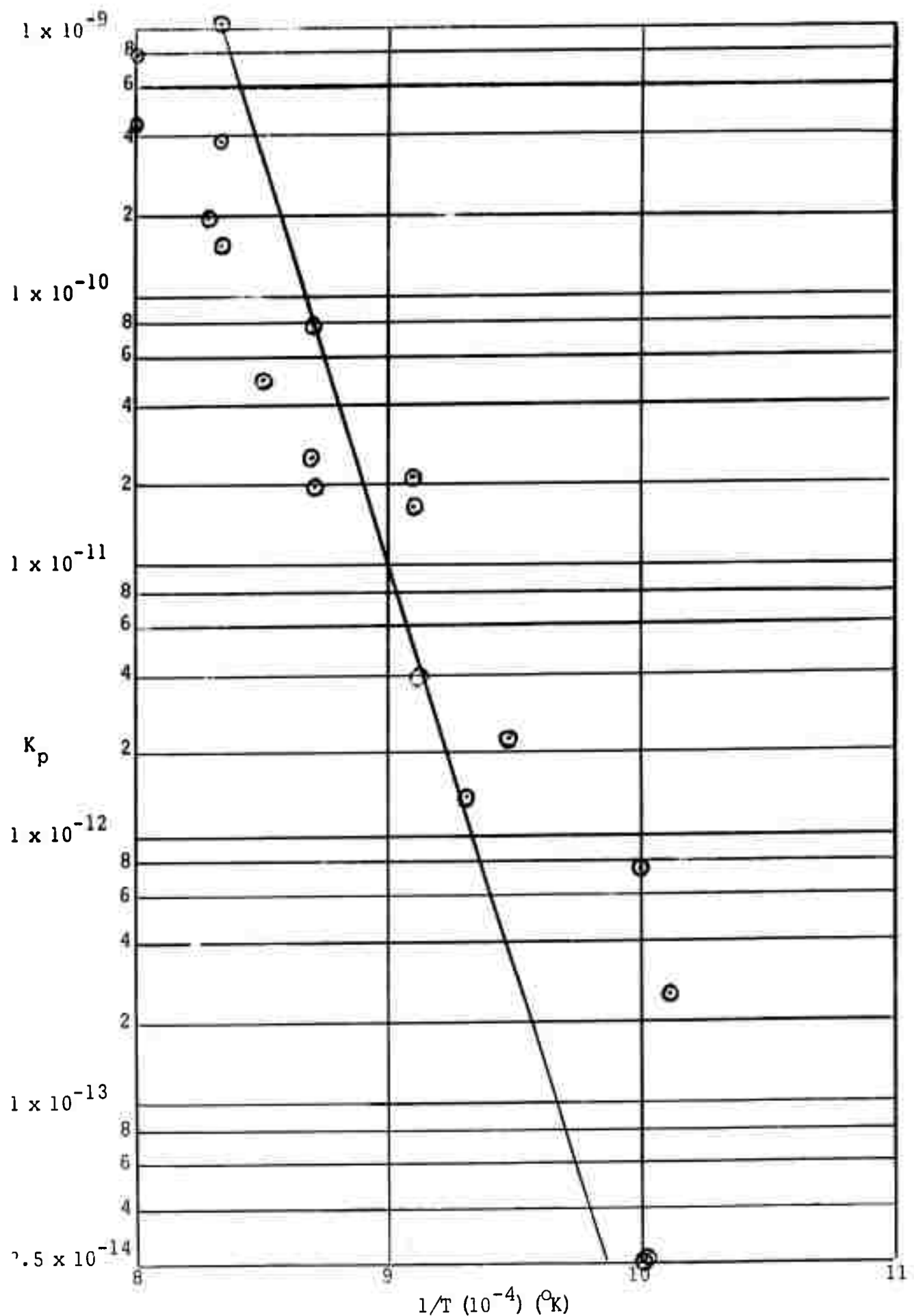


Fig. 1. The logarithm of K for the equilibrium $\text{B}_2\text{O}_3 (\text{l}) + \text{BF}_3 (\text{g}) = 3\text{BOF} (\text{g})$ as a function of $1/T$.

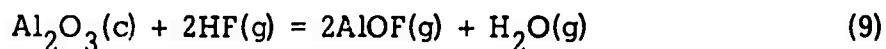
III. FUTURE WORK

Experiments will be undertaken to determine the heat of formation of AlOF and concurrently, studies of the molecular flow reaction method will continue. The determination of the heat of formation of AlOF, however, will take first priority.

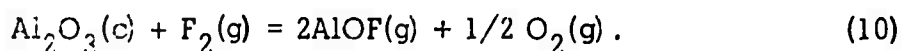
The heat of formation of AlOF can be determined directly by several methods. These include transpiration, effusion, and possibly the molecular flow reaction method (7). A preliminary study will be made of the reactions and experimental methods which are listed in the following paragraphs in order to determine which one will be best suited to give a definitive value of the heat of formation of AlOF.

1. Transpiration

The transpiration method currently employed for the BOF studies and described in reference (6) may be used to study the reaction,



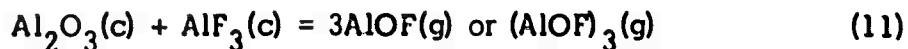
and



The apparatus and experimental procedure will be essentially the same as that described in reference (6) with the exception that the reaction tube must be made of nickel instead of quartz.

2. Effusion Experiments

The boiling point of AlF_3 is given in the literature as slightly over 1500°K (10) while the dissociation of Al_2O_3 does not occur to any extent below 2500°K (11). Therefore, an effusion experiment in the range of 1000 to 1500°K can be performed with a mixture of crystalline Al_2O_3 and AlF_3 undergoing the reaction,

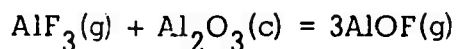


The gas over the crystalline compounds in the effusion cell will contain a mixture of the monomer AlOF, the trimer (AlOF)₃ and possibly some vaporized AlF₃. However, in certain temperature ranges, the concentration of the monomer or trimer will be in a negligible amount.

3. Molecular Flow Reaction Method

The heat of formation of BOF given in this report was obtained by the molecular flow reaction method. In using this method it is necessary to assume that the accommodation or evaporation coefficient is equal to unity. It is considered that this is a good assumption, but in order to check this point molecular flow experiments will be made on HBO₂. Meschi, Chupka and Berkowitz (12) have studied HBO₂ by mass spectrometry and a check with their data should prove the reliability of this method.

A molecular flow experiment can be performed for AlOF by passing AlF₃ over Al₂O₃. The experiment would consist of placing a boat containing Al₂O₃ and an effusion cell containing AlF₃ in an evacuated quartz tube. The flow rate of the AlF₃ is determined by the orifice size and the temperature of the effusion cell. The equilibrium constant for the reaction



is determined gravimetrically and analytically.

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