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UNITED STATES ATOMIC ENERGY COMMISSION  
FORMATION OF METHYL BORATE FROM THE  
METHYL BORATE-BORON FLUORIDE COMPLEX.

By  
D. A. McCaulay  
W. L. Rittschof

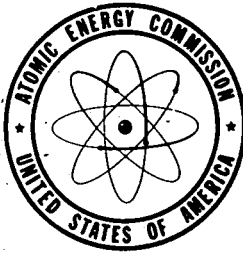
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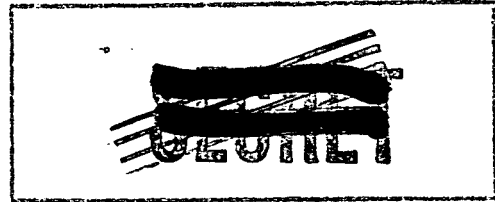
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STANDARD OIL COMPANY (INDIANA)

No. 4 Process Laboratory



Classification

File No. 512

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This document consists of 5 pages and 1 figures. (This cover sheet is page 1.)

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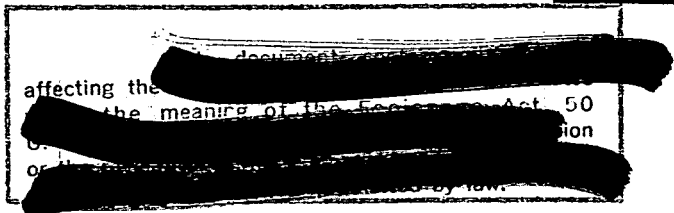
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M R E P O R T

Formation of Methyl Borate  
From the Methyl Borate-Boron Fluoride Complex

by D. A. McCaulay and W. L. Rittschof

Summary

In a previous report<sup>1</sup> the existence of the following equilibrium was established,

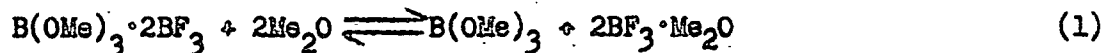


Since it appeared that loss of boron into the vacuum system of the fractionation unit could easily result from displacement of the equilibrium to the right by the presence of free methyl ether in the unit, an investigation of the extent of this possible displacement was undertaken. Methyl ether was bubbled through boiling methyl borate-boron fluoride complex and the vapors were rectified. It was found that the overhead product consisted mainly of methyl borate and that the residue consisted of methyl ether-boron fluoride complex.

The results of this investigation indicate that the reaction goes to completion under these conditions and that the occurrence of this reaction could account for the high losses of boron from the fractionation unit which have been observed at various times.

Introduction

It has been shown from vapor pressure measurements made in this laboratory<sup>1</sup> that methyl ether and methyl borate-boron fluoride complex react reversibly to form methyl ether-boron fluoride complex as shown in the following equation,



The measured equilibrium constant for reaction (1) was small, and there is, therefore, little tendency for the above reaction to proceed to the right except under the influence of a large excess of one of the reactants and the continuous removal of one of the products. Thus, if a large excess of ether is present, the reaction should be displaced to form methyl borate, which if continuously removed might be formed until all the methyl borate complex was used up.

If this occurred in the plant fractionation unit it would explain losses into the vacuum system which were sometimes greater than accountable by flow of vent gas and vapor pressures of material thought to be present.

<sup>1</sup>Report No. A-2354.

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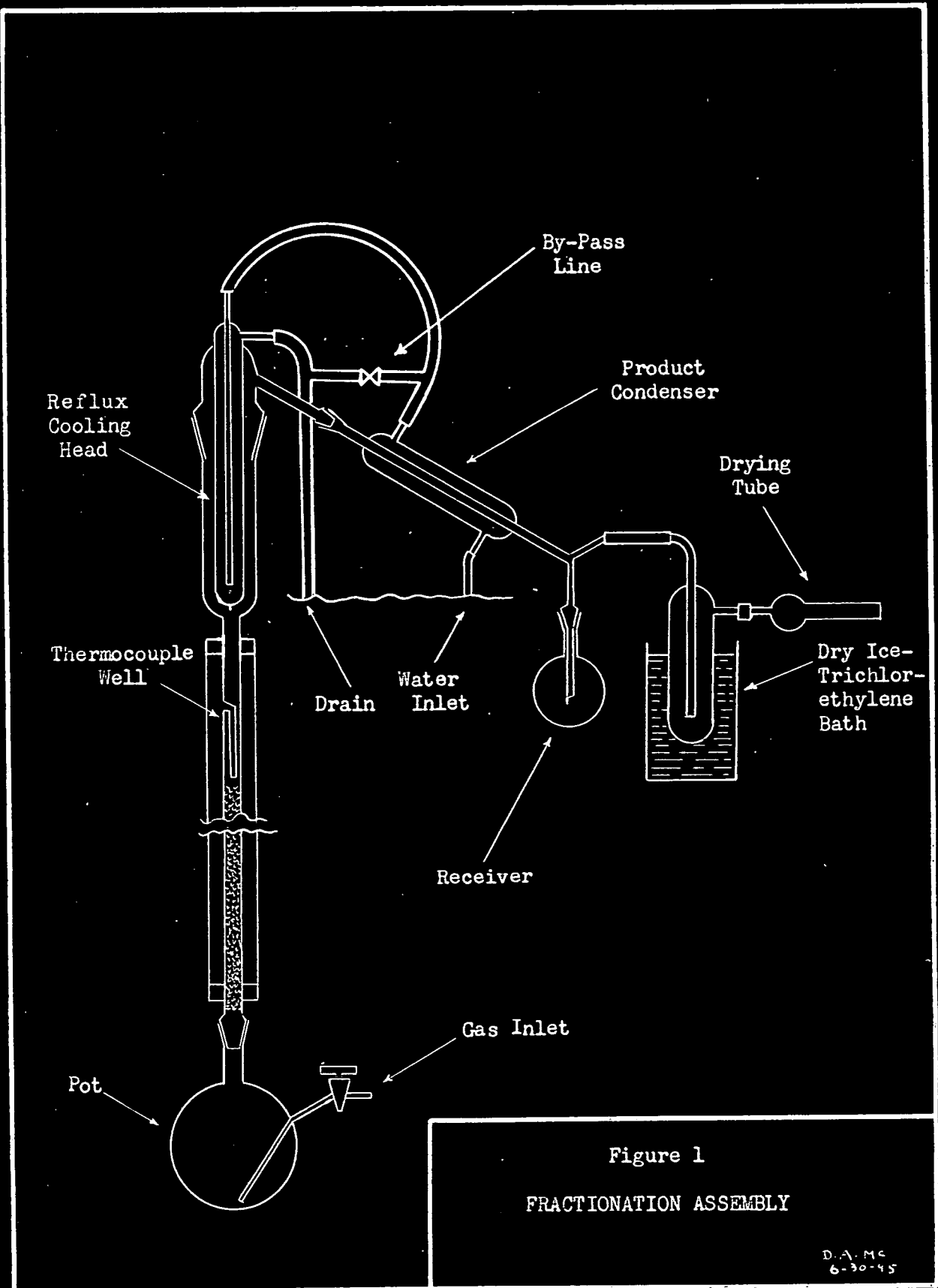


Figure 1  
FRACTIONATION ASSEMBLY

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An excess of ether might be present in the columns of the fractionation unit if the ether complex were contaminated with water or if an excess of ether were present in the entering feed. Under these conditions it is probable that the volatile methyl borate would be carried into the vacuum system.

It was the purpose of this investigation to devise an experiment which would simulate plant conditions when an excess of ether was present and thus would measure roughly the extent to which the methyl borate complex would be lost.

### Apparatus

The apparatus used consisted mainly of a fractionating column fitted with a tube for admitting gas to the still pot. A schematic drawing of the apparatus is given in Figure 1, and a description of the essential parts is given in the following paragraphs:

- a. Still Pot - The pot was a 300 ml. round bottom flask fitted with a gas inlet tube which reached almost to the bottom and with a female ground glass joint for connecting it to the column.
- b. Column - The column was made from a length of 15 mm. pyrex glass tubing on the lower end of which was sealed a male ground glass joint for the still pot connection and on the upper end a short length of 25 mm. tubing and a female ground joint for the connection to the reflux condenser. The column was packed to a height of 21 inches with 5/32 inch I.D. single turn glass helices and was estimated to have approximately seven theoretical plates. Above the packed space but below the reflux condenser was sealed a thermocouple well in which was placed an iron-constantan thermocouple well for measuring the overhead temperature.
- c. Reflux Condenser - The reflux condenser consisted of a cold finger made from 15 mm. pyrex tubing and a male ground glass joint for connecting it to the column. The reflux rate was controlled by the amount of cooling water allowed to flow through the reflux condenser and was measured by the rate at which drops fell from the bottom of the cold finger.
- d. Product Condenser - The product condenser was a conventional all-glass type fitted with ground glass joints for connection to the vapor delivery arm of the column and to the receiver.

### Procedure

The methyl borate complex used was material which had been collected from the vacuum lines of the fractionation unit. Before use, it was purified by distillation in the column described above and was found to have a boiling point of 87°C. and a freezing point of 39°C. These constants agreed with those given in the literature for the complex.

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The methyl borate complex was placed in the pot which was then attached to the column. Tank methyl ether was slowly bubbled through the liquid while the pot heater was adjusted to effect moderate refluxing. Cooling water was regulated to give an approximate two to one reflux ratio.

Distillation was continued until a drop in the overhead temperature indicated that all the methyl borate had distilled over. A sample of the pot residue was analyzed for boron and fluorine<sup>2</sup>, for per cent ether complex by ether evolution<sup>3</sup>, for Karl Fischer water<sup>4</sup>, and for specific resistance. The distillate was analyzed for methyl borate by treating a sample with an excess of boron fluoride, measuring the increase in weight, and identifying the resulting product as the methyl borate-boron fluoride complex by a melting point determination.

Data

The data obtained are as follows:

1. Starting Material - Methyl borate-boron fluoride complex

Voluns = 200 ml.  
Boiling point = 87°C.  
Freezing point = 39°C.

2. Overhead Product

Volume = 90 ml.  
Boiling range = 52°C. to 57°C. (740 mm. Hg.)  
Wt. of sample = 11.5433 g.  
Wt. of BF<sub>3</sub> added = 12.8135 g.  
Wt. of methyl borate in sample based on wt. of BF<sub>3</sub> added = 9.80 g.  
Per cent methyl borate in sample = 85.0%  
Melting point of derivative = 37-39°C.

3. Pot Residue

Voluns = 200 ml.  
Boiling point = 127°C. (740 mm. Hg.)  
Per cent ether complex from boron analysis = 99.4%  
Per cent ether complex from fluorine analysis = 99.3%  
Per cent ether complex from ether evolution = 99.3%  
Per cent Karl Fischer water = 0.98  
Specific Resistance = 1683 ohms

<sup>2</sup>SAM Report A-1299.

<sup>3</sup>SAM Report A-2120, p. 48.

<sup>4</sup>SAM Report M-1184, p. 3.

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### Discussion

Chemical analysis of the residue shows that it is practically one hundred per cent methyl ether-boron fluoride complex formed in amounts roughly predicted by equation (1).

The analysis of the distillate shows that it is 85% methyl borate. Also, the fact that the derivative obtained on treating the distillate with boron fluoride exhibits a melting point only slightly lower than that of pure methyl borate-boron fluoride complex, indicates that most of the remaining 15% of the distillate is methyl borate-boron fluoride complex.

From these results, therefore, it is apparent that the methyl borate complex has been converted into the methyl ether complex which remains in the pot and into the volatile methyl borate which distills over.

The same conditions under which this experiment was carried out might from time to time exist in the plant columns. Thus, whenever water leaks into the system, the formation of methyl borate complex is accelerated<sup>5</sup> and methyl ether is liberated. The methyl borate complex and methyl ether then react to form methyl borate which distills out of the condenser into the vacuum line. It is quite probable, therefore, that the formation and vaporization of methyl borate account for the high loss of boron into the vacuum system.

### Conclusions

1. It has been demonstrated that under the proper conditions, methyl borate complex and methyl ether will react quantitatively to form methyl ether complex and methyl borate. The conditions required are a large excess of methyl ether and continuous removal of the methyl borate formed.

2. It is concluded that the abnormally high loss of boron from the plant fractionation unit observed at various times may be accounted for by this reaction.

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<sup>5</sup>Report to be issued.

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