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Report No. A-2363

A STUDY OF THE REACTIONS OF METHYL ETHER-BORON-FLUORIDE COMPLEX
WITH WATER UNDER FRACTIONATION CONDITIONS

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A STUDY OF THE REACTIONS OF METHYL ETHER-BORON FLUORIDE COMPLEX
WITH WATER UNDER FRACTIONATION CONDITIONS

A. SUMMARY

Experiments were carried out in a glass column in order to investigate the reactions of methyl ether-boron fluoride complex with water under fractionation conditions.

It was demonstrated that for each mole of water added:

- 1) one mole of complex is decomposed
- 2) one-half mole of ether is recovered in the gas collecting system
- 3) one-half mole of ether disappears
- 4) one-half mole of water disappears
- 5) .06 mole of methyl borate-boron fluoride complex is formed in excess of that resulting from thermal decomposition

In order to explain these reactions, the following equations are postulated:

The last equation would account for the etching of the still pot which was also observed.

It is recognized that these reactions may not be identical with those occurring in the plant fractionation unit because of differences in materials of construction and in method of operation. Nevertheless, the conclusions obtained should be helpful in explaining some of the phenomena occurring in the plant and it is recommended that the data be given further study.

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B. INTRODUCTION

Experimental distillations of mixtures of methyl ether-boron fluoride complex and water were originally undertaken in connection with the fractionation unit at this location (1) in an attempt to find a method of recovering pure methyl ether-boron fluoride complex from complex contaminated with water. The investigation comprised a series of nine experimental runs in which the overhead cuts and the column bottoms were subjected to resistivity measurements, were analyzed for per cent water by the Karl Fischer method, for purity by evolution of methyl ether and in certain cases for per cent of elements boron and fluorine. The conclusions which were reached on the basis of these runs are discussed fully in a previous report (2). Since these earlier experiments led directly to the extended and more detailed investigation presented in this report, a brief summary of the conclusions is given as follows:

1. Separation of pure ether complex from mixtures of ether complex and water may be conveniently accomplished by distillation.

2. Karl Fischer analyses, resistance measurements and purity analyses indicate that water and other impurities concentrate in the first and last overhead fractions and in the column bottoms, thus making it necessary to take a "heart cut" in the distillation.

3. The addition of water to ether complex results in the formation of at least two compounds, one of which is more volatile than complex, and the other of which is less volatile.

4. Comparison of the data with SAM Laboratory correlations of conductivity versus Karl Fischer water content indicated that the overhead fractions contain a greater mole per cent of OH than of H while the bottoms contain a greater mole per cent of H than of OH.

During the course of this work it became apparent that the experimental technique, suitably modified, could be used for a more detailed study of the reactions of methyl ether complex with water in order to obtain a better understanding of what happens under fractionation conditions. As indicated above, the earlier experiments had given qualitative information but had not yielded any quantitative data which might make it possible to determine the actual reactions occurring between water and ether complex. Experiments at the SAM Laboratories (3) had shown that Karl Fischer "water" disappears upon heating water and complex in a closed system. Other experimental work was also in progress at the SAM Laboratories, some of which was completed during the course of this investigation (4)(5), while other results became available after this investigation had been completed (6). At the time the experiments presented in this report were planned, there were a number of questions to which specific answers had not been found, for example:

1. What is the relationship between water content and decomposition rate under continuous fractionation conditions?

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2. What happens to water in the methyl ether complex-water system, particularly when it can no longer be found by Karl Fischer analysis?

3. What is the quantitative relationship between water added and methyl ether liberated?

4. Is the decomposition reaction which takes place in the presence of water identical with thermal decomposition? If not, what are the products formed and at what rate are they formed?

To answer these questions, experimental work was planned which, broadly, was devoted to obtaining quantitative data on the nature and extent of the chemical reactions occurring between methyl ether complex and water under conditions simulating plant fractionation. It was realized that data could be obtained more rapidly if the experiments were carried out in a simple apparatus, such as a one-plate equilibrium still. However, it was felt that if any of the reaction products required more than one or two plates for complete separation from the ether complex, the results in a one-plate fractionation might not be at all indicative of what would happen in the plant fractionation unit, where a large number of plates are available to make sharp separations between reaction products. For these reasons, it was deemed necessary to simulate plant conditions as closely as possible, which required the use of the column employed in previous experiments, together with the necessary additional equipment to make it possible to determine quantities of all products, including gaseous constituents. The experiments were carried out at 150 millimeters of mercury pressure using the same vacuum control system which had been used for the previous runs.

Minor modifications and refinements in method were made in order to accomplish the desired results, based on the experience obtained in the previous experimental runs. All materials charged to the column and removed from the column were weighed on an analytical balance, or the weights accurately determined indirectly. Fractions were analyzed for per cent water by the Karl Fischer method, for per cent methyl ether-boron fluoride complex by Me_2O evolution, and for per cent of elements boron and fluorine. Specific resistance measurements were made whenever possible. With the exception of one run, the column was operated essentially at total reflux in order to duplicate as closely as possible the extremely high reflux ratios being employed in the plant unit. It was necessary, however, to remove small amounts of material overhead to avoid clogging of the lines with solid decomposition products, but it was not found desirable to complicate the experiments by taking large overhead fractions, which would result in concentration of the bottoms.

Because of the large number of fractions of material sampled, and the extensive analyses desired on these fractions, a long period of time was required to complete the analytical results and work up the data. During this period, results became available from the SAM Laboratories (4) (5) from which a number of interesting conclusions had been drawn:

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1. It was found that boric acid dissolved in ether complex is more volatile than the complex itself. (In other work at this laboratory it was found that this was due to reaction of boric acid with complex to form other compounds(7).)

2. Apparent rates of decomposition determined by the static manometric method indicated that a definite correlation could be drawn between the apparent decomposition rate and the water added to the complex. It was also found that iron salts greatly increased the decomposition rates. However, there was some uncertainty in interpreting these data since it was necessary to make assumptions as to the composition of the gas evolved.

3. Experiments in a monel Stedman packed distillation column indicated that rates of decomposition as measured by methyl fluoride evolution rose to about 4% per day upon addition of water.

4. It was found that once the monel Stedman column had been contaminated with salts due to reaction of wet complex with metals in the system, the decomposition rates remained at about 4% per day even when dry complex was used. It was found extremely difficult to clean the system thoroughly enough to obtain normal decomposition rates (less than 1% per day) with dry complex.

These results obtained by the SAM Laboratories are of interest since when coupled with the results obtained in the experiments described below, they should make it possible to obtain a more complete understanding of the reactions of methyl ether complex with water. However, in view of the fact that it has been possible to keep water leakage into the fractionation unit down to a very small amount over a period of more than six months, this problem has not been sufficiently urgent to warrant the detailed study of the data necessary in order to reach all the conclusions which might be drawn. Nevertheless, it has been possible to draw a number of clear-cut conclusions from these experiments which are definitely of value in understanding the reactions of ether complex with water. It is strongly recommended that these data together with the data obtained at the SAM Laboratories be given very careful study before any further work is done on the reactions of ether complex with water.

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Figure 2

VACUUM CONTROL SYSTEM

Figure 1

DISTILLATION COLUMN

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C. APPARATUS

The complete fractionation apparatus and the accessory equipment used in obtaining the data of this report have already been described in detail in a previous report (2). The fractionation system consisted of a distillation column equipped with a distilling head connected to the overhead take-off system and to the gas collecting traps, a specially built graduated receiver with conductivity cell attachment, a still pot and heating device (Figure 1) and a vacuum control system (Figure 2).

The distillation column shown in Figure 1 was 1/2 inch in diameter, and was packed to a height of 38 inches with 5/32 inch I.D. single-turn glass helices. The column contained approximately twelve theoretical plates based on data presented in the previous report.

The vacuum control system, Figure 2, consisted of two interconnected systems maintained at different pressures. One of the pressure systems was connected to the column and receiver and controlled accurately to 150 millimeters of mercury pressure; the other system, which served as a vacuum reservoir, was controlled roughly between 10 and 100 millimeters pressure.

The gas collection system was connected to the distilling head of the column between stopcock K (Figure 1) and line A of the vacuum control system (Figure 2) and was designed to permit the collection and transfer of gaseous materials from the run without interrupting the progress of the run. It consisted essentially of two nitrogen cooled traps connected in parallel to permit the isolation of either one of the traps while the gas from the run collected in the other trap. Both traps were provided with side exits through which they could be evacuated independently of the central system and through which the contents could be removed for analysis.

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D. PROCEDURE

The fractionation runs were carried out according to the following procedure:

1. Preliminary to starting the run, the column and receiver were flushed with ether and dried, stopcocks greased, and the dewar flasks surrounding the traps were filled with liquid nitrogen.

2. With stopcocks K and L (Figure 1) closed to the column, the vacuum control system was started with manostat G (Figure 2) adjusted to give a column side pressure of 150 mm. of mercury $\pm$ 0.2 mm. The pump side pressure was maintained somewhere between 10 and 100 mm. of mercury.

3. A measured amount of methyl ether-boron fluoride complex was poured into the still pot and the weight obtained on a laboratory scale to $\pm$ 0.1 grams. A few boiling chips were added and the pot was connected to the column, as in Figure 1.

4. Stopcocks K and L were opened gradually as the system was adjusted to the control pressure of 150 mm. of mercury.

5. After the column pressure had been adjusted, a known amount of water was added to the complex in the still pot. This was done, dropwise, by means of a weighing burette which was conveniently connected to the stopcock on the side of the still pot by means of a ground glass joint.

6. The heating element in the oil bath was turned on and temperature of the bath was adjusted to give the desired boil-up rate.

7. The column was brought to equilibrium by being held at total reflux.

8. Small amounts of overhead material were taken over into the graduated receiver at various times throughout the course of the runs. Each overhead fraction was transferred directly into the evacuated conductivity cell through the stopcock D (Figure 1). Without removing the conductivity cell, the resistance in ohms was read from a conductivity bridge and the temperature measured by means of a thermometer hanging alongside the conductivity cell.

9. To remove the conductivity cell with its contents, the vacuum in the cell was broken by opening the capillary bleed and admitting dry air. The cell was stoppered, and the part of the joint attached to the apparatus was stoppered with a standard taper ground glass female joint.

10. The conductivity cell was weighed on an analytical balance. The contents were emptied into a dried sample bottle and set aside for analyses of per cent water by Karl Fischer, per cent complex by Me_2O evolution and for per cent of boron and fluorine.

11. Gaseous products of the run were collected in one of the two nitrogen traps and were removed when desired during the course of the runs. This was done by isolating the trap containing the gas sample and directing the gas from the column through the second nitrogen trap. The gaseous material in the first trap was then removed and expanded in a calibrated system of the usual design.

12. At the end of the run, the heat was shut off and the system was allowed to cool to room temperature. The still pot, which then contained both the column bottoms and the column drainings, was weighed on a laboratory scale to $\pm .1$ gram, emptied into a dried sample bottle and saved for analyses of per cent water by Karl Fischer, per cent ether complex by Me_2O evolution and for element analyses of boron and fluorine.

13. Throughout the course of each run a record was kept of the overhead vapor temperature, temperature of the complex in the still pot, resistivity of the contents of the still pot, oil bath temperature, column temperature, reflux ratio and the time corresponding to each measurement.

E. ANALYTICAL METHODS

The analytical methods employed in the determination of weight per cent water by the Karl Fischer procedure, weight per cent methyl ether-boron fluoride complex by Me_2O evolution, weight per cent of elements boron and fluorine and the measurement of specific resistance have already been described in other reports (2)(8).

The boron analyses are reported to three significant figures. However, in the case of fluorine, it was discovered after the completion of the analyses that a faulty step had caused an error in most of the fluorine determinations.(8) For this reason, all fluorine analyses have been omitted from this report. Nevertheless, the mole ratios of F/B calculated from the separate boron and fluorine analyses have been included, since in a number of instances even approximate results are of value in interpreting the data. In those instances where the fluorine determinations are known to have been obtained by the correct method of analysis, the mole ratio of F/B is given to three significant figures. Where the determinations for fluorine are in doubt, the mole ratio of F/B is given to only two significant figures.

Gas analyses for volume per cent Me_2O , boron fluoride and methyl fluoride were made according to the procedure developed in this laboratory(9). During the process of removing a sample of gas from the expansion system for analyses, it was observed that, after freezing down with liquid nitrogen and reexpanding the gas, a small amount of liquid remained in the bulb. This occurred whenever the gas was frozen down with liquid nitrogen and reexpanded, and the liquid was not readily volatilized at room temperature. This phenomenon led to an investigation of the system methyl ether and methyl borate-boron fluoride complex (10). It was concluded that the liquid was methyl borate-boron fluoride complex which had been carried into the gas phase by the large quantities of methyl ether present under conditions of the experiments. Such small quantities of the methyl borate complex, however, are not believed to have an appreciable effect on the results of the gas analyses.

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F. DATA AND RESULTS

The data obtained are to be found in the Appendix in Tables I to XVII. The four fractionation experiments presented in this report are summarized in Table I. These consist of Runs 14, 16, 17 and 18. Run 15 was unsuccessful and was repeated as Run 16. All of the runs were made with fresh "plant feed" complex taken directly from the feed preparation unit. In three of the runs, water was deliberately added. The fourth was made without added water.

In Run 14 the contents of the still pot were sampled and analyzed about every six hours. The fractionation column was operated at total reflux during the course of the day and was shut down for the night. The still pot was sampled the next morning before starting up. With the exception of 6.5 grams of methyl borate-boron fluoride complex which were withdrawn after 10.3 hours, the column was kept at total reflux for a total of 47-1/2 hours. Thereafter, five overhead fractions were withdrawn and analyzed.

In Runs 16, 17 and 18 small amounts of overhead material (mostly methyl borate-boron fluoride complex as evidenced by the low overhead vapor temperature and by Me_2O evolution analyses) were taken over into the graduated receiver at various times throughout the course of the runs. Only one overhead fraction was taken in each of Runs 16, 17 and 18.

Summaries of the operating data are given in Tables II, IV, VI and VIII. Included are such data as progress of the run in hours, overhead vapor temperatures, still pot content temperatures and resistance data for still pot contents.

The analytical data for the runs are presented in Tables III, V, VII and IX. Included are the results of the analytical procedures for per cent water, purity of the complex by Me_2O evolution, and specific resistance, together with the assumptions and estimations necessary in the interpretation of these data.

Table X presents the element analyses which include boron analyses and the mole ratios of fluorine to boron for all the runs. Other data for the same fractions are repeated for comparative purposes.

Table XI contains the data obtained from gas analyses and includes the calculated weight, in grams, of the condensable gases.

Table XII presents a comparison of the quantities of methyl ether evolved upon addition of water to the ether complex with the theoretical quantities expected.

The calculated composition of the system in Run 14 after 13.0 hours of operation is given in Table XIII. Data for the calculations were obtained from Table III and the purpose of the table is to make possible a direct comparison with the shorter runs.

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The results of calculations of the overall decomposition of methyl ether-boron fluoride complex due to the presence of water are presented in Table XIV.

Calculations of the rate of formation of methyl fluoride are contained in Table XV.

Table XVI shows the effect of water upon the ratio of methyl fluoride to methyl borate complex observed.

Table XVII presents a calculated breakdown of the decomposition of ether complex into thermal decomposition and additional decomposition to form methyl borate complex without evolution of methyl fluoride.

Some of the data have also been plotted in Figures 3 to 9. Figures 3 and 4 present the data from Table XIV on decomposition of ether complex.

Figure 5 shows the formation of methyl borate complex, taken from Table XVII.

In Figure 6, the overhead vapor temperatures for all the runs have been plotted against the time in hours.

Figures 7 and 8 present the analyses of column bottoms for Run 14 taken over a period of time.

Figure 9 compares specific resistances and Karl Fischer water analyses of column bottoms with the SAM Laboratory correlations.

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G. DISCUSSION OF RESULTS

1. General

An examination of the data in Tables III, V, VII and IX indicates that good material balances have been obtained for all of the runs, as summarized below. The weight per cent material recovery includes the static hold-up of the column, which was assumed to be 5.0 grams.

Material Balance

<u>Run Number</u>	<u>Grams Input</u>	<u>Grams Output</u>	<u>Wt. % Recovery</u>
14	257.3	247.9	96.3
16	257.5	253.2	98.3
17	250.4	247.5	98.8
18	179.5	178.4	99.4

As may be seen in the analytical data tables, a number of estimations and assumptions were necessary for each of the runs in order to make the data complete. As indicated, these assumptions were made on the basis of other experimental data from the runs, and are deemed justifiable in view of the fact that such small amounts of material were involved.

The total lengths of Runs 16, 17 and 18 were 18.1, 12.9 and 13.3 hours, respectively, and were thus roughly comparable with regard to the decomposition for the total length of the run. No water was added to the ether complex in Run 18, hence this run served as a control run for comparison of the decomposition with the other runs. Run 14 was 53.4 hours in length, or almost four times as long as the other runs. This difference in hours of operation should be kept in mind when comparing directly the data of Run 14 with the data of the other three runs. Nevertheless, it was possible to compare the data of Run 14 with the data of the other runs since chemical analyses had been obtained about every six hours throughout the progress of the run. In Table XIII the composition of Run 14 has been calculated after 13.0 hours of operation to place it on an equivalent time basis with Runs 16, 17 and 18.

2. Decomposition of Methyl Ether-Boron Fluoride Complex due to Water

An examination of the pertinent data in Tables III, V, VII, IX and XIII, which are summarized in Table XIV, indicated quantitatively the major decomposition occurring when water is contacted with ether complex under conditions simulating plant fractionation at 150 mm. of Hg. The results are presented graphically in Figures 3 and 4.

The overall major results of the addition of one mole of water are:

- 1) the loss of one mole of complex as determined by the Me_2O evolution method

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Figure 5

PRODUCTION OF METHYL BORATE COMPLEX

E.N.H.
D.A.M.
10/1/45

Figure 4

LOSS OF METHYL ETHER

Moles Water Added to Ether Complex

REDFIELD & ESSER CO., N. Y. NO. 369-14
 Multiplex, 5 mm. lines spaced, cm. lines heavy.
 MADE IN U.S.A.

E.N.H.
 D.A.M.
 10/1/45

19

Figure 3

20

NEOPOL & ESSER CO., N. Y. NO. 350-14
Milliliters, 5 mm. line accepted, cm. line heavy.
MADE IN U.S.A.

E.N.H.
D.A.M.
10/1/45

21

22

23

Figure 9

COMPARISON OF SPECIFIC RESISTANCE AND KARL FISCHER DATA FOR COLUMN BOTTOMS
WITH S.A.M. LABORATORY CORRELATIONS (REPORT NOS. M-1184 AND M-11405)

Specific Resistance at 25°C., ohms $\times 10^3$

$\times 10^2$

$\times 10^4$

KEUFFEL & ESSER CO., N. Y. NO. 359-1261
Logarithmic, 3 1/2 Cycles.
MADE IN U.S.A.

E.N.H.
D.A.M.
10/1/45

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- 2) the loss of one-half mole of water as determined by the modified Karl Fischer water procedure
- 3) recovery of one-half mole of ether in the gas collecting system
- 4) the loss of one-half mole of ether by difference

Included in Figures 3 and 4 are the theoretical straight lines with the slopes corresponding to the mole for mole and mole for one-half mole reactions. It will be noted that all of the curves, with the exception of the one for the loss of water are shifted to the right of the theoretical lines and are roughly parallel to them. This shift is explained first, by the fact that less than 100 per cent material was recovered, and second, by the fact that in addition to the decomposition due to water a certain amount of "thermal" decomposition takes place whenever ether complex is held at fractionation conditions at 150 mm. Hg.

In order to study the "thermal" decomposition occurring during these experiments, the rate of formation of methyl fluoride has been calculated for each run, as shown in Table XV. It will be recalled that "thermal" decomposition takes place according to the following equation, established by the SAM Laboratories (11).

Using this equation, the "thermal" decomposition rates were calculated from the rates of evolution of methyl fluoride for all runs except No. 14 in which all of the methyl fluoride was not collected. These decomposition rates appear to be substantially independent of the amount of water added, averaging 2.6% per day. It is of interest that these rates are intermediate between the rate of less than 1% per day determined for "dry" complex in a clean column and 4% per day determined for "wet" or "dry" complex in a monel column contaminated with metal salts.(5)

It also appeared desirable to compare the formation of methyl borate complex with the formation of methyl fluoride as a check on whether equation (A) was a true representation of the decomposition occurring. These data have been calculated as the ratio of methyl fluoride to methyl borate complex, as shown in Table XVI. It is evident from this table that Run 18 is the only one which even closely approaches the theoretical ratio of 3 moles of methyl fluoride per mole of methyl borate complex, as called for by equation (A). Evidently the addition of water to complex results in the production of abnormally high quantities of methyl borate complex. In order to investigate this point more fully, the total moles of methyl borate complex has been plotted against the water added, as shown in Figure 5. Also, the data have been recalculated in Table XVII in order to segregate "thermal" decomposition and "additional" decomposition to form methyl borate complex without the formation of methyl fluoride. In making these calculations, it was assumed that the data for Run 18

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Figure 6

OVERHEAD VAPOR TEMPERATURES

Legend

- Run 18 (0% water added)
- Run 17 (2.46% water added)
- Run 14 (4.64% water added)
- Run 16 (4.87% water added)

Overhead Vapor Temperature °C.

Time in Hours

57

E.N.H.
D.A.M.
10/1/45

KEUFFEL & ESSER CO., N. Y. NO. 350-14
Millimeters, 5 mm. lines accepted, cm. lines heavy.
MADE IN U.S.A.

KRUPP & ESSER CO., N. Y. NO. 350-14
MILWAUKEE, 5 inch. Pipe Section, 100 lb. heavy.
MADE IN U. S. A.

Figure 7

PROGRESSIVE EXAMINATION OF
THE STILL BOTTOMS - RUN 14

E.N.H.
D.A.M.
10/1/45

Figure 8

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were representative of the thermal decomposition occurring during all the runs. This may be somewhat high, as indicated in Table XV, but is suitable for approximate calculations. The results of these calculations indicate that the formation of excess methyl borate complex is proportional to the amount of water added and is approximately .06 mole of methyl borate complex per mole of water added. Thus, the presence of water in the complex does not appear to have a direct effect on reaction (A), but results in a reaction to form small amounts of methyl borate complex unaccompanied by the formation of methyl fluoride. However, it does appear that the "thermal" decomposition reaction has been catalyzed in some way during these runs, presumably by decomposition products of water and complex which are present in the still pot. Such catalysis has been observed due to the presence of metal salts in a distillation column (5), but it is not known just what material could have catalyzed the reaction in this case. In any event, it appears that two reactions, "thermal" decomposition, and the production of additional methyl borate^{complex} by water may be considered to be taking place simultaneously and independently when methyl ether complex reacts with water under fractionation conditions.

3. Rate of Reaction of Methyl Ether-Boron Fluoride Complex with Water

In each of the runs in which ether complex was contacted with water, the evolution of methyl ether took place almost immediately on heating. In every case this evolution was complete after one hour. Following the liberation of ether, the overhead temperatures decreased gradually, as may be seen from Figure 6, which is plotted from the data contained in the operating summaries. In each case where water was added, the overhead temperature became constant at 60°C. after approximately three hours. This is due to the accumulation of methyl borate-boron fluoride complex, which boils at 60.4°C. at 150 mm. Hg. Thus, while the complete evolution of ether takes place almost immediately, the reaction to form excess methyl borate complex takes place relatively slowly.

From an examination of Figures 7 and 8 it is evident that, after approximately the first six hours at total reflux in run 14, the water content by Karl Fischer, the purity of the complex by ether evolution, and the specific resistance reach a steady state and remain remarkably constant until distillate is withdrawn. This appears to indicate that the reactions whereby ether complex is decomposed by water are essentially complete after six hours. After withdrawal of overhead is started the composition of the material in the still pot changes in proportion to the amount of distillate removed. This last observation is in agreement with the experiments reported previously.(2)

Another observation which confirmed the results of the original work was the presence of a greater mole per cent of H than of OH in the column bottoms material as evidenced by specific resistances which were much lower than would be expected from the Karl Fischer water content using existing correlations. This is demonstrated in Figure 9 in which the specific resistances for all column bottoms materials are plotted against the Karl Fischer water content of the samples. All of the values fall below the lowermost curve of the SAM Laboratory correlations. (3)(4) Evidence of the presence of HF was also found in these runs, as indicated by etching of the still pot.

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4. Postulated Chemical Equations for the Reactions of Methyl Ether-Boron Fluoride Complex with Water

Any chemical equations postulated for the reactions of ether complex with water under conditions simulating those of the fractionation unit must explain the quantitative findings of this investigation. These are, for the addition of a mole of water to excess complex:

- 1) the loss of one mole of complex, as determined by the ether evolution procedure,
- 2) the recovery of one-half mole of the ether in the gas collecting system,
- 3) the disappearance of one-half mole of ether by difference,
- 4) the disappearance of one-half mole of water, as determined by the modified Karl Fischer procedure, and
- 5) the production of 0.06 mole of methyl borate complex in excess of that formed by "thermal" decomposition.

In addition, the reactions offered should also account for the presence of material contributing to conductivity, which does not appear to be water, and for the presence of a small amount of HF.

In Runs 14, 16 and 17, an amount of methyl ether was collected in the liquid nitrogen cooled traps which leads to the postulation of equation (B):

Thus, even though the overall loss of ether is mole for mole of water added, the recovery, which is essentially complete during the first hour of operation, indicates the initial formation of boron fluoride dihydrate. (See Table XII and Figure 4.) Inspection of equation (B) shows that it accounts for half of the complex lost in 1) and for all of the ether recovered. Also, the water present is in a form that is quantitatively found by the Karl Fischer procedure. It is necessary, then, to postulate a further reaction, or reactions which will account for the loss of another half mole of complex, half of the added water and the half mole of ether displaced in this further decomposition. These conditions are fulfilled by equation (C):

In (C) the disappearance of half a mole each of water and of ether is accomplished by conversion to methyl alcohol which forms a complex with the boron fluoride available. Since it has not been possible to find a boron-oxygen linkage other than an ester linkage which was not found as "water" by the Karl Fischer determination, (8) the postulation of the methyl alcohol appears to be a reasonable explanation of the disappearance of water and of ether from a glass fractionation

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system in which no bottoms product is withdrawn. Furthermore, if the right-hand side of the equation (C) is thought to exist as $H^+BF_3OMe^-$ and $H_3O^+BF_3OMe^-$ it is apparent that more ionizing material is present than would be explained by Karl Fischer water-conductivity correlations. Thus, equations (B) and (C) are consistent with the first four findings listed above and in addition offer a suggestion for the excess of H over OH observed in the column bottoms.

Since the amount of methyl borate-boron fluoride complex formed due to the presence of water in the complex is small, its presence could be explained by a reaction such as:

This would also account for the etching of the glass still pot observed in all cases with boiling, wet complex under conditions approaching those in the unit.

Equations (B), (C), and (D) are consistent with the findings of this investigation and are postulated as the reactions which appear to be taking place. However, it must be realized that the reactions in the plant fractionation unit are not necessarily identical. The main points of difference are that the unit is operated as a producing cascade and is constructed of metal rather than of glass. Thus, while it has been shown in a glass column operated at substantially total reflux that the disappearance of water upon heating mixtures of methyl ether complex and water may be accompanied by an increase in methyl alcohol, by the Karl Fischer alcohol determination, no such correlation has been observed in the plant. (8)

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H. CONCLUSIONS

1. Under conditions simulating those in plant operation, an investigation of the reactions of methyl ether-boron fluoride complex with water in glass apparatus has given quantitative information concerning the decomposition of this complex. Thus, it has been demonstrated that for each mole of water added:

- (a) one mole of complex is decomposed
- (b) one-half mole of ether is recovered in the gas collecting system
- (c) one-half mole of ether disappears
- (d) one-half mole of water disappears
- (e) 0.06 mole of methyl borate-boron fluoride complex is formed in excess of that resulting from thermal decomposition

2. Equations for reactions suggested by the quantitative data obtained from this investigation are postulated. These are:

in which the formation of methanol is advanced as a possible explanation for the simultaneous disappearance of equal molar quantities of ether and of water. The first reaction appears to take place within the first hour, while the second appears to be complete after six hours.

3. The formation of methyl borate in excess of that found by thermal decomposition may be explained by the following postulated reaction:

This would also account for the presence of HF in wet complex.

4. It is recognized that the reactions suggested to explain the results obtained in glass apparatus are not necessarily identical with those occurring in the plant fractionation unit because of differences in materials of construction and in method of operation.

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I. APPENDIX

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TABLE II

Operating Summary of Run 14

Time in Hours	Progress of the Run	Material Withdrawn		Overhead Vapor Temp. °C.	Material in the Still Pot		
		Sample Number	Wt. in Grams		Temp. °C.	Measured Resistance, ohms	Spec. Res. at 25°C., ohms*
0	11.93 grams water added to 246.0 grams of Plant feed ether com- plex. Heat on.	-	-	-	27.3	32.5	121
0.10	--	-	-	-	48.4	20.0	96
0.35	--	-	-	-	69.2	16.0	93
0.42	--	-	-	-	86.8	12.8	86
0.62	--	-	-	-	95.5	10.5	75
0.7	--	-	-	89.3	96.8	10.0	72
1.0	Gaseous material in trap removed by expansion to a gas bulb as 14T1.	14T1	18.202	81.6	97.0	9.5	69
1.2	--	-	-	71.0	97.0	9.5	69
2.3	--	-	-	60.0	97.2	8.1	59
4.7	--	-	-	60.0	97.2	6.8	49
5.9	--	-	-	60.0	97.2	6.8	49
5.9	1st portion of column bottoms removed.	14B1	10.166	-	18.8	14.4	47
6.8	--	-	-	60.0	97.2	6.7	49
7.3	Gaseous material in trap removed by expansion to a gas bulb as 14T2.	14T2	[.5]	-	-	-	-
7.3	Liquid remaining in bulb removed as 14R2.	14R2	[3.]	-	-	-	-
10.3	Started taking off small amount of overhead which was almost pure methyl borate complex.	14-1	6.400	60.0	97.2	6.7	49
11.0	--	-	-	85.0	97.2	6.5	47
13.0	--	-	-	85.0	97.2	6.5	47
13.0	2nd portion of column bottoms removed.	14B2	10.743	-	17.8	13.8	45
14.3	--	-	-	84.0	96.8	6.5	47
20.3	--	-	-	77.0	96.8	6.5	47
20.3	3rd portion of column bottoms removed.	14B3	11.980	-	16.2	13.9	44
23.1	--	-	-	84.5	96.4	6.5	47
28.8	--	-	-	87.0	96.2	6.5	47
28.8	4th portion of column bottoms removed.	14B4	14.290	-	19.2	13.3	44

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TABLE I
Summary of Runs

Run No.	Duration of Run, Hours	Charge					
		<u>Plant Feed Methyl Ether- Boron Fluoride Complex</u>				<u>Total Water In Charge</u>	
		<u>Ether Complex, Grams</u>	<u>Wt. % Water by Karl Fischer</u>	<u>Water Added</u>		<u>Grams</u>	<u>Wt. %</u>
14	53.4	245.4	.073	11.93	4.64	12.11	4.71
16	18.1	245.0	.073	12.54	4.87	12.72	4.94
17	12.9	244.2	.073	6.17	2.46	6.35	2.53
18	13.3	179.5	.073	0	0.0	.13	0.07

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TABLE II (Cont'd.)

Time in Hours	Progress of the Run	Material Withdrawn		Overhead Vapor Temp. °C.	Material in the Still Pot		
		Sample Number	Wt. in Grams		Temp. °C.	Measured Resistance, ohms	Spec. Res. at 25°C., ohms*
28.8	Gaseous material in trap removed by expansion to a gas bulb as 14T3.	14T3	1.16	-	-	-	-
28.8	Liquid remaining in the bulb and trap removed as 14R3.	14R3	9.883	-	-	-	-
30.3	--	-	-	85.0	96.6	6.3	45
35.5	--	-	-	76.0	95.3	6.3	45
35.5	5th portion of column bottoms removed.	14B5	12.567	-	18.4	14.1	46
38.0	--	-	-	77.0	97.2	6.3	46
42.8	Gaseous material in trap removed by expansion to a gas bulb as 14T4.	14T4	[.5]	79.5	97.2	6.3	46
42.8	Liquid remaining in bulb removed as 14R4.	14R4	1.645	-	-	-	-
42.8	6th portion of column bottoms removed.	14B6	15.506	-	19.2	13.4	44
47.6	2nd overhead cut completed.	14-2	17.980	91.3	96.1	-	-
48.5	3rd overhead cut completed.	14-3	17.157	91.0	98.6	-	-
48.8	--	-	-	90.4	100.1	-	-
49.5	4th overhead cut completed.	14-4	18.427	88.6	102.5	-	-
50.2	5th overhead cut completed.	14-5	10.893	90.0	104.5	-	-
50.2	Gaseous material in trap removed by expansion to a gas bulb as 14T5.	14T5	[.5]	-	-	-	-
50.2	7th portion of column bottoms removed.	14B7	11.602	-	-	-	-
53.4	6th overhead cut completed.	14-6	12.414	90.0	104.5	-	-
53.4	End of run. Remainder of column bottoms removed.	14B8	37.426	-	-	-	-
	Total material	-	243.0	-	-	-	-

*Temp. coefficient of resistance = .014 ohms/°C. as used in A-2353; Cell constant = .278

[] Estimated weights.

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Sample Number	Description of Material	Time in Hr. After Start of Run	Grams*** Methyl Borate Complex	Moles Methyl Borate Complex	Specific Resistance at 25°C., ohms
Charge*	(245.40 grams feed ether complex) (11.93 grams water added) (257.33 grams total)	0	-	-	121
14B1	1st column bottoms sample	5.0	-	-	-
14B2	2nd " " "	13.0	-	-	-
14B3	3rd " " "	20.0	-	-	-
14B4	4th " " "	28.0	-	-	-
14B5	5th " " "	35.0	-	-	-
14B6	6th " " "	42.0	-	-	-
14B7	7th " " "	50.0	-	-	-
14B8	8th " " "	53.0	-	-	25
	Total Bottoms	5			
14-1	1st Overhead Cut	10.0	5.34	.022	-
14-2	2nd " "	47.0	2.32	.010	1500
14-3	3rd " "	48.0	0.35	.001	3830
14-4	4th " "	49.0	0.37	.002	3040
14-5	5th " "	50.0	0.51	.002	1640
14-6	6th " "	53.0	0.94	.004	875
	Static Hold-up**	-1	0.38	.002	-
	Total Overheads	5	10.21	.043	
14T1	Gaseous content of 1st gas sample	1.0	-	-	-
14T2	Gaseous " " 2nd " "	7.0	-	-	-
14R2	Liquid " " 2nd " "	7.3	2.7	.011	-
14T3	Gaseous " " 3rd " "	28.0	-	-	-
14R3	Liquid " in traps	28.0	8.85	.037	-
14T4	Gaseous " of 4th gas sample	42.0	-	-	-
14R4	Liquid " " 4th " "	42.0	1.5	.006	-
14T5	Gaseous " " 5th " "	50.0	-	-	-
	Total Traps	3	13.1	.054	
	Combined Totals	6	23.3	.097	
	Material Loss	9	-	-	249

*Analysis of plant feed ether complex charge:

0.073% water by Karl Fischer

100% ether complex by Me₂O evolution

1760 ohms, Specific Resistance at 25°C.

**Static hold-up of column assumed to be equal to other complex and methyl

***Calculated from per cent complex by Me₂O evolution ether complex and methyl borate complex on the basis of gaseous samples

[] Estimated weights.

[] Composition of static hold-up assumed to be the other runs. (See Table XI.)

and per cent ether complex

is of bottoms samples 14B4

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TABLE IV

Operating Summary of Run 16

Time in Hours	Progress of the Run	Material Withdrawn		Overhead Vapor Temp. °C.	Temp. of Material in Still Pot °C.
		Sample Number	Wt. in Grams		
0	12.54 grams water added to 245.0 grams Plant feed ether complex, heat on.	-	-	-	25
0.8	--	-	-	89.0	94.0
0.9	--	-	-	88.0	95.0
1.0	--	-	-	86.0	95.0
1.2	--	-	-	78.5	95.0
1.3	--	-	-	71.3	95.0
1.5	--	-	-	64.5	95.0
1.6	--	-	-	62.0	-
2.0	--	-	-	60.5	-
2.6	--	-	-	60.0	-
4.3	Gaseous material in trap removed by expansion to a gas bulb as 16T1.	16T1	18.49	60.0	96.7
4.3	Liquid remaining in bulb removed as 16R1.	16R1	[.3]	-	-
5.1	Methyl borate complex freezes up the overhead take-off system.	-	-	60.0	97.5
5.5	Starting here small amounts of overhead were taken into re- ceiver as 16-1, and continued to the end of the run.	16-1	23.55	-	-
9.5	--	-	-	91.0	97.2
11.3	Gaseous material in trap removed by expansion to a gas bulb as 16T2.	16T2	.405	87.5	97.2
11.3	Liquid remaining in bulb removed as 16R2.	16R2	[.4]	-	-
18.1	End of run. Gaseous material in trap removed by expansion to a gas bulb as 16T3.	16T3	.345	85.0	97.2
18.1	Liquid remaining in bulb removed as 16R3.	16R3	.407	-	-
18.1	Liquid material remaining in the traps after completion of the run.	16R4	1.74	-	-
	Column Bottoms removed.	16B	202.6	-	25
	Total Material		248.2		

[] Estimated Weights.

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Sample Number	Description of Material	Time in Hr After Start of Run	Moles Methyl Borate Complex	Grams MeF	Moles MeF	Specific Resistance at 25°C. ohms
Charge*	(245.0 grams feed ether complex) (12.54 grams water added) (257.54 grams total charge)	0	-	-	-	-
16T1	Gaseous content of 1st gas sample	4.	-	.762	.0224	-
16R1	Liquid " " 1st " "	4.	.0011	-	-	-
16T2	Gaseous " " 2nd " "	11.	-	.348	.0102	-
16R2	Liquid " " 2nd " "	11.	.0015	-	-	-
16T3	Gaseous " " 3rd " "	18.	-	.276	.0081	-
16R3	Liquid " " 3rd " "	18.	.0015	-	-	-
16R4	{ Liquid remaining in the traps } { after completion of the run }	18.	.0065	-	-	-
16-1	{ Total overhead withdrawn } { throughout the run }	18.	.0494	-	-	4330
16-B	Column Bottoms	18.	-	-	-	43
	Static Hold-up*		.0013	-	-	-
	Totals		.0613	1.386	.0407	-
	Material Loss					

- *Same as in Table III.
- []¹Estimated weights.
 - []²Karl Fischer water and per cent ether comp of overhead cuts Run 14.
 - []³Assumed to have the same per cent ether comp sample 14R3, Run 14.
 - []⁴Karl Fischer water in gaseous materials as

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TABLE VI

Operating Summary of Run 17

Time in Hours	Progress of the Run	Material Withdrawn		Overhead Vapor Temp. °C.	Temp. of Material in Still Pot °C.
		Sample Number	Wt. in Grams		
0	6.173 grams water added to 244.2 grams of feed ether complex, heat on.	-	-	-	25
0.8	--	-	-	87.5	93.5
1.1	--	-	-	84.3	-
1.5	--	-	-	70.0	93.9
1.8	--	-	-	64.0	93.9
2.8	Solid methyl borate complex freezes out along the water condenser. Small amounts of overhead were started into the receiver as 17-1 and continued to the end of the run.	17-1	33.608	61.0	93.9
2.9	Switched to trap II. Gaseous material in Trap I removed by expansion to a gas bulb as 17T1.	17T1	9.875	-	-
2.9	Liquid remaining in bulb removed as 17R1.	17R1	[.2]	-	-
12.9	End of run. Gaseous material in Trap II removed by expansion to a gas bulb as 17T2.	17T2	.608	91.0	94.8
12.9	Liquid remaining in bulb removed as 17R2.	17R2	.264	-	-
12.9	Liquid material remaining in the traps after completion of the run.	17R3	2.079	-	-
	Column Bottoms removed	17B	195.9	-	25
	Total Material		242.5		

[] Estimated weight.

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Sample Number	Description of Material	Time in Hr. After Start of Run	Moles Methyl Borate Complex	Grams MeF	Moles MeF	Specific Resistance at 25°C., ohms
Charge*	(244.2 grams feed ether complex) (<u>6.17</u> grams water added) (250.4 grams total charge)	0	-	-	-	-
17T1	Gaseous content of 1st gas sample	2.9	-	.275	.0081	-
17R1	Liquid " " 1st " "	2.9	.0008	-	-	-
17T2	Gaseous " " 2nd " "	12.9	-	.525	.0154	-
17R2	Liquid " " 2nd " "	12.9	.0010	-	-	-
17R3	{Liquid remaining in the traps} {after completion of the run }	11.8	.0078	-	-	-
17-1	{Total overhead withdrawn} {throughout the run }	12.9	.0259	-	-	2560
17-B	Column Bottoms	12.9	-	-	-	66
	Static Hold-up*		.0008	-	-	
	Totals		.0363	.800	.0235	

Material Loss

*Same as in Table III.

- [] ¹Estimated weights.
- [] ²Karl Fischer water and per cent ether content of overhead cuts Run 14.
- [] ³Assumed to have the same per cent ether content as Sample 14R3, Run 14.
- [] ⁴Karl Fischer water in gaseous materials

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TABLE VIII
Operating Summary of Run 18

Time in Hours	Progress of the Run	Material Withdrawn		Overhead Vapor Temp. °C.	Temp. of Material in Still Pot °C.
		Sample Number	Wt. in Grams		
0	179.5 grams ether complex charged, heat on.	-	-	-	25
0.7	--	-	-	89.3	91.1
1.2	--	-	-	88.5	93.5
1.9	--	-	-	87.8	93.5
2.9	--	-	-	87.0	93.5
4.3	--	-	-	85.2	93.5
5.5	--	-	-	83.2	93.5
6.2	Gaseous material in trap removed by expansion to a gas bulb as 18T1.	18T1	1.315	82.7	93.5
6.2	Liquid material remaining in bulb removed as 18R1.	18R1	.253	-	-
7.3	--	-	-	80.0	93.1
10.2	--	-	-	76.2	93.1
12.9	Small amounts of overhead were started into the receiver as 18-1, and continued to the end of the run.	18-1	9.193	70.8	93.1
13.3	End of run. Gaseous material in trap removed by expansion to gas bulb as 18T2.	18T2	.571	91.0	93.1
13.3	Liquid material remaining in bulb removed as 18R2.	18R2	.264	-	-
	Column Bottoms removed	18B	<u>161.8</u>	-	25
	Total Material		<u>173.4</u>		

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TABLE X

Element Analyses

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Sample No.	Designation of Material	Wt. % B by Element Analysis	Mole Ratio F/B	Wt. % Water by Karl Fischer	Wt. % Ether Complex by Me ₂ O Evolution	Specific Resistance at 25°C., ohms
14B1	Column Bottoms 1	9.28	3.2	2.51	67.8	47
14B2	Column Bottoms 2	9.51	3.0	2.77	69.3	45
14B3	Column Bottoms 3	-	-	2.96	69.8	44
14B4	Column Bottoms 4	9.31	3.1	3.02	69.1	44
14B5	Column Bottoms 5	9.42	3.0	3.13	62.8 (?)	46
14B6	Column Bottoms 6	9.42	3.1	3.47	69.3	44
14B7	Column Bottoms 7	9.57	3.22	8.78	47.1	-
14B8	Column Bottoms 8	9.56	3.22	14.9	37.7	25
14R2	Trap 2 Liquid	-	2.13	-	-	-
14R3	Trap 3 Liquid	11.65	1.85	.09	10.4	-
14-1	Overhead Cut 1	12.90	2.1	.03	-	-
14R4	Trap 4 Liquid	12.28	1.9	-	-	-
14-2	Overhead Cut 2	10.00	2.8	1.67	87.1	1500
14-3	Overhead Cut 3	9.71	3.0	.338	98.0	3830
14-4	Overhead Cut 4	9.83	2.9	.273	98.0	3040
14-5	Overhead Cut 5	9.75	2.9	.634	95.3	1640
14-6	Overhead Cut 6	10.08	2.8	2.20	92.4	875
16-1	Overhead Cut 1	11.52	2.4	1.34	49.8	4330
16-B	Column Bottoms	9.65	3.1	3.48	70.3	43
16R1	Trap 1 Liquid	-	2.3	-	-	-
16R2	Trap 2 Liquid	-	1.7	-	-	-
16R3	Trap 3 Liquid	-	1.2	-	-	-
16R4	Trap 4 Liquid	12.19	2.1	-	-	-
17R2	Trap 2 Liquid	-	1.88	-	-	-
17R3	Trap 3 Liquid	12.19	2.1	-	-	-
17-1	Overhead Cut 1	10.54	2.7	0.72	81.5	2560
17-B	Column Bottoms	9.57	3.0	1.36	81.3	66
18R1	Trap 1 Liquid	-	2.3	-	-	-
18R2	Trap 2 Liquid	-	2.23	-	-	-
18-1	Overhead Cut	10.51	2.7	1.16	76.5 (?)	2730
18-B	Column Bottoms	9.54	3.0	.011	100.0	318
Theo- retical	Me ₂ O·BF ₃	9.50	3.00	0	100	Mol. Wt. 113.8
	B(OMe) ₃ ·2BF ₃	13.55	2.00	0	0	239.4
	BF ₃ ·2H ₂ O	10.42	3.00	34.6	0	103.8
	BF ₃ ·(Me) ₂ O·2HF	7.03	5.00	0	0	153.8
	HBF ₄	12.32	4.00	0	0	87.8
	B(OMe) ₃	10.42	0.00	0	0	103.8

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TABLE XI

Analysis of Gases

Sample Number	Volume in cc.	Temp. °C.	mm. Hg. Pressure	Volume % by Gas Analysis			Condensable Gases				
				Me ₂ O	MeF	Non- Condensables	Calc. Wt. in Grams			Calc. Wt. %	
							Me ₂ O*	MeF*	Total	Me ₂ O	MeF
14T1	-	-	-	-	-	-	[17.47]	[.73]	18.202**	[96]	[4]
14T2***	-	-	-	0.0	92.2	0.0	0.0	[.46]	[.5]	0	85.5
14T3	790	27.0	715	7.6	92.4	0.0	.116	1.04	1.16	10	90
14T4	-	-	-	25.0	75.0	0.0	[.17]	[.33]	[.5]	[34]	[66]
14T5	-	-	-	52.0	48.0	0.0	[.35]	[.15]	[.5]	[70]	[30]
16T1	11,837	30.7	652	94.5	5.5	0.0	17.73	.762	18.49	95.9	4.1
16T2	860	25.4	246	10.9	90.1	0.0	.057	.348	.405	14.1	85.9
16T3	364	25.0	523	14.6	79.2	6.2	.069	.276	.345	20.0	80.0
17T1	12,331	26.0	330	95.5	3.7	0.8	9.60	.275	9.875	97.2	2.8
17T2	865	24.8	392	9.9	84.6	5.5	.083	.525	.608	13.6	86.4
18T1	873	26.5	712	58.3	37.3	4.4	.893	.422	1.315	67.9	32.1
18T2	863	25.0	358	3.4	96.4	0.2	.026	.545	.571	4.5	95.5

*Calculated from gaseous volume, pressure, and temperature, using the gas laws.

**Frozen gas weighed on analytical balance.

***This sample contained 7.8 volume % (or 14.5 wt. %) of BF₃

[] Estimated values.

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Sample Number	Description of Material	Time in Hrs After Start of Run	les thyl rate mplex	Grams MeF	Moles MeF	Specific Resistance at 25°C., ohms
Charge	179.5 grams feed ether complex	0	-	-	-	1760
18T1	Gaseous content of 1st gas sample	6.2	0010	.422	.0124	-
18R1	Liquid " " 1st " "	6.2	-	.545	.0160	-
18T2	Gaseous " " 2nd " "	13.3	0010	-	-	-
18R2	Liquid " " 2nd " "	13.3	-	-	-	-
13-1	{Total overhead withdrawn} throughout the run	13.3	0090	-	-	2730
18B	Column Bottoms	13.3	-	-	-	318
	Static Hold-up*	-	0000	-	-	-
	Totals	-	0110	.967	.0284	-

Material Loss

*Same as in Table III.

☐ ¹Estimated weights.

☐ ²Karl Fischer water and per cent ether complex data for overhead cuts Run 4, Figure 5, R

☐ ³Assumed to have the same per cent ether complex sample 14R3, Run 14.

☐ ⁴Karl Fischer water in gaseous materials assumed

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TABLE XII

Evolution of Methyl Ether Gas by the Addition
of Water to Methyl Ether-Boron Fluoride Complex

Run Number	Time in Hours Me ₂ O Gas Collected	Grams Ether Complex Charged to Run	Grams Water Added to Run	Grams Me ₂ O Gas Collected	Theoretical Grams Me ₂ O*	
					For 1 mole water liberating 1 mole Me ₂ O	For 1 mole water liberating 1/2 mole Me ₂ O
14	1.0	245.4	11.93	17.30	30.6	15.3
16	4.3	245.0	12.54	17.73	32.1	16.0
17	2.9	244.2	6.17	9.60	15.8	7.9
18	6.2	129.5	0.00	0.89	0.0	0.0

*Calculated for $\text{Me}_2\text{O} \cdot \text{BF}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{O} \cdot \text{BF}_3 + \text{Me}_2\text{O}$

and $\text{Me}_2\text{O} \cdot \text{BF}_3 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{O} \cdot \text{BF}_3 + \text{Me}_2\text{O}$

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TABLE XIII

Composition of Run 14 after 13.0 hours*

<u>Material</u>	<u>Time in Hrs. After Start of Run</u>	<u>Wt. in Grams</u>	<u>Wt. % Water by Karl Fischer</u>	<u>Grams Water</u>	<u>Moles Water</u>	<u>Wt. % Ether Complex by Me₂O Evolution</u>	<u>Grams Ether Complex</u>	<u>Moles Ether Complex</u>	<u>Grams Me₂O</u>	<u>Moles Me₂O</u>
Charge	0	257.3	4.70	12.106	.672	-	245.4	2.155	99.3	2.155
14T1	1.0	18.20	-	-	-	-	-	-	17.47	0.380
14B1	5.9	10.12	2.51	.254	.014	67.8	6.86	.060	2.77	0.060
14T2	7.3	0.5	-	-	-	-	-	-	-	-
14R2	7.3	3.0	.09	.003	.000	10	.30	.003	.12	.003
14-1	10.3	6.4	.03	.002	.000	16.5	1.06	.009	.43	.009
Remainder	13.0	<u>219.1</u>	2.77	<u>6.069</u>	<u>.337</u>	69.3	<u>151.84</u>	<u>1.333</u>	<u>61.42</u>	<u>1.333</u>
Combined Total		257.3		6.328	.351		160.06	1.405	82.21	1.785
Material Loss				5.778	.321		85.34	.750	17.1	.370

*Calculated from data in Table III.

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TABLE XIV

Decomposition of Methyl Ether-Boron Fluoride Complex Due to Water

Run Number	Moles Water Added	Moles Me ₂ O Lost			Moles of Ether Complex Lost**	Moles of Water Lost***	Moles Lost/Moles H ₂ O Added				
		Total	Evolved as Gas	Non-Re-*** coverable			Me ₂ O Total	Me ₂ O Evolved as Gas	Me ₂ O Non-Re- coverable	Of Ether Complex	Of Water
14	.662	.816	.380	.436	.816	.131	1.233	.574	.659	1.233	.198
14*	.662	.750	.380	.370	.750	.321	1.133	.574	.559	1.133	.485
16	.696	.752	.385	.367	.752	.297	1.080	.553	.527	1.080	.427
17	.343	.458	.208	.250	.458	.190	1.335	.606	.729	1.335	.554
18	.00	.048	.019	.029	.048	.0003	-	-	-	-	-

*Calculated compositions after 13.0 hours of run operation (Table XIII).

**By Me₂O evolution analysis.

***By Karl Fischer analysis.

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TABLE XV

Rate of Formation of Methyl Fluoride

Gas Sample Number	Moles Ether Complex Charged to Run	MeF Produced			Moles MeF/hour	Moles MeF/Hour/Mole Ether Complex Charged	Thermal Decomp. Rate Per cent/Day**
		Time in Hours	Wt. in Grams	Moles			
14T3*	--	21.5	1.04	.0306	.00142	-	
16T1		4.3	.762	.0224			
16T2		7.0	.348	.0102			
16T3		6.8	.276	.0081			
Run 16 Total	2.151	18.1	1.386	.0407	.00224	.00104	2.50
17T1		2.9	.275	.0081			
17T2		10.0	.525	.0154			
Run 17 Total	2.144	12.9	.800	.0235	.00182	.00085	2.03
18T1		6.2	.422	.0124			
18T2		7.1	.545	.0160			
Run 18 Total	1.576	13.3	.967	.0284	.00214	.00136 .00108 (Avg.)	3.26 2.59

*The weights of the other gas samples in Run 14 were not obtained.

**Calculated from MeF evolution rate assuming $3\text{Me}_2\text{O} \cdot \text{BF}_3 \longrightarrow \text{B}(\text{OMe})_3 \cdot 2\text{BF}_3 + 3\text{MeF}$

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TABLE XVI

Ratios of Methyl Fluoride to
Methyl Borate-Boron Fluoride Complex Observed

<u>Run Number</u>	<u>Duration of Run, Hours</u>	<u>Mols Water Added</u>	<u>Mols Ether Complex Charged to Run</u>	<u>Wt. of Methyl Borate Complex</u>	<u>Mols Methyl Borate Complex</u>	<u>Mols MeF</u>	<u>Mols MeF/Mols Methyl Borate Complex</u>
14	53.4	0.663	2.155	23.3	.0970	-	-
16	18.1	0.696	2.151	14.72	.0613	.0407	0.664
17	12.9	0.343	2.144	8.70	.0363	.0235	0.647
18	13.3	0.00	1.576	2.63	.0110	.0284	2.582

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TABLE XVII

Thermal Decomposition and Additional
Decomposition due to Water

Run Number	Moles Ether Complex Charged to Run	Time in Hours	For Total Run			Thermal Decomposition			Additional Decomposition	
			Moles Water Added	Moles MeF	Moles Methyl Borate Complex	Moles* Methyl Borate Complex	Moles MeF/Moles Methyl Borate Complex		Moles** Methyl Borate Complex	Moles Methyl Borate Complex /Moles H ₂ O Added
14	2.155	53.4	.662	-	.0970	.0604	-		.0366	.0553
16	2.151	18.1	.696	.0407	.0613	.0204	2.00		.0409	.0588
17	2.144	12.9	.343	.0235	.0363	.0145	1.62		.0218	.0636
18	1.576	13.3	.000	.0284	.0110	.0110	$\frac{2.58}{2.07}$ (avg.)		.0000	$\frac{-}{.0592}$ (avg.)

*Calculated from the methyl borate complex produced in Run 18, assuming this was due to thermal decomposition only. This gave a rate of .000525 moles of methyl borate complex per hour per mole of ether complex charged.

**Total moles methyl borate complex minus moles methyl borate complex by thermal decomposition.

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