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For The Atomic Energy Commission

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Chief, Declassification Branch TC

EXCHANGE METHOD OF PREPARING BORON TRIFLUORIDE SAMPLES
FOR MASS SPECTROMETER ANALYSIS OF DIMETHYL ETHER-BORON TRIFLUORIDE

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ERRATA FOR REPORT A-2358

The following changes should be made in report A-2358, "Exchange Method of Preparing Boron Trifluoride Samples for Mass Spectrometer Analysis of Dimethyl Ether-Boron Trifluoride", by Charles M. Judson, October 23, 1945:

1. The second and third paragraphs on page 20 should be changed to read:

"The fact that only 40% of the theoretical amount of boron is converted to BF_3 in the routine procedure is one possible source of error. It is not unreasonable to assume that there is an isotopic fractionation in the process of dissociation (9):

If isotopic fractionation takes place in the same manner as all other reactions of boron compounds which have been studied, the gas will be enriched in B^{11} .

In order to estimate the magnitude of this additional discrepancy the equilibrium constant for reaction (10):

is assumed to be of the same order of magnitude as that reaction in (3), that is about 1.027. Using the Rayleigh equation for the distillation of 40% to the vapor phase with an equilibrium constant of 1.027, if the initial concentration is 95.0 atom per cent B^{10} the gas taken off will be 94.9 atom per cent B^{10} . In this case a correction of 0.1% for this fractionation would be applied to all determinations made in the 95 per cent range by the calcium fluoride conversion procedure. Making such a correction the discrepancy between the two methods of preparing gas samples is reduced from 0.3 per cent to 0.2 per cent."

2. On page 15 at the end of the next to the last paragraph, the phrase "to include both of these values" should be omitted.
3. On page 16 at the end of the next to the last paragraph, "Table III" should be changed to read "Table II".

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A new procedure for the preparation of BF_3 samples for the mass spectrometer determination of B^{10} abundance in $(\text{CH}_3)_2\text{O}:\text{BF}_3$ is described. A measured amount of previously analysed BF_3 gas is brought to equilibrium with the $(\text{CH}_3)_2\text{O}:\text{BF}_3$ to be analysed. After equilibrium has been established, the gas is analysed and the abundance of B^{10} calculated. Using this method in conjunction with the null method of spectrometer analysis, accurate determinations can be made rapidly. Validity of the exchange procedure has been demonstrated by measurements of the rate at which equilibrium is approached and by an experimental verification of the calculated equilibrium constant for the exchange of boron isotopes between BF_3 gas and liquid $(\text{CH}_3)_2\text{O}:\text{BF}_3$. A comparison with the conversion procedure used heretofore in which $(\text{CH}_3)_2\text{O}:\text{BF}_3$ was converted into $\text{CaF}_2:\text{BF}_3$ and then into BF_3 gas indicates a slight but definite discrepancy between the two methods which has been attributed to errors in the CaF_2 procedure. In the course of the examination of the methods for preparing mass spectrometer samples, consideration has been given to the precision of the mass spectrometer measurements.

In the research on methods for the separation of the isotopes of boron,¹ and in the operation of a plant for the fractionation of boron isotopes in which dimethyl ether-boron trifluoride was used,² it was necessary to develop methods for the determination of the abundances of boron isotopes. In the early stages of the research at the S.A.M. Laboratories of Columbia University, a heavy metal mass spectrometer was used. Two mass spectrometers specially constructed for measurements with boron isotopes were designed on the basis of observations made with the heavy metal mass spectrometer. These instruments have been used for measurements with boron trifluoride gas and with trimethyl borate vapor. The construction and operation of these instruments, one of which has been used in this laboratory, has been described by Inghram.³

For isotopic analyses of dimethyl ether-boron trifluoride complex a procedure for the conversion of this complex into boron trifluoride gas was developed by Kirshenbaum.¹ In this procedure the $(\text{CH}_3)_2\text{O} \cdot \text{BF}_3$ is allowed to react with an excess of CaF_2 at 70°C ., according to equation (1):

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On heating to a higher temperature the $\text{CaF}_2\text{:BF}_3$ dissociates and the BF_3 is recovered. Following Kirshenbaum's procedure it was necessary to allow eight hours for the reaction with CaF_2 . For plant control analyses this procedure was found to be unduly lengthy.

It was found that very rapid analyses could be made by a method not employing a mass spectrometer. This method is being described in another report.⁴ After using this "rapid method" it became apparent that analyses of high accuracy could be obtained more easily with the mass spectrometer than with the "rapid method" if the BF_3 gas for the mass spectrometer could be prepared readily.

A procedure in which a measured amount of previously analysed BF_3 gas is brought to isotopic equilibrium with the $(\text{CH}_3)_2\text{O:BF}_3$ to be analysed was found to provide a sufficiently rapid method. By using BF_3 gas with an isotope abundance approximately equal to that of the $(\text{CH}_3)_2\text{O:BF}_3$ to be analysed, the time required to reach equilibrium is shortened and the correction which must be applied to take account of the effect of the added BF_3 on the isotope abundance of the mixture is small.

Exchange equilibrium methods have been used in mass spectrometer analyses with other elements. Cohn and Urey⁵ used equilibration with CO_2 in the measurement of the O^{18} content of heavy water. Equilibration with H_2 gas has also been used in the measurement of deuterium in heavy water. This method was studied in detail at S.A.M. Laboratories.⁶

To prove the reliability of the exchange method of preparing samples, experiments were carried out to show that equilibrium is reached in a very short time, and that the same equilibrium is reached on starting with gas with an abundance of B^{10} both higher and lower than that in the liquid phase. Experiments in which this procedure was compared with the original CaF_2 conversion procedure indicated a discrepancy of about 0.3% in the analysis of 95 atom % B^{10} . Detailed examination of the situation indicated that the error lay in the CaF_2 conversion procedure.

Two corrections are necessary in making the calculations of isotope abundances when using the exchange method. First a correction must be made for the difference between the abundance in the gas phase which was analysed and that in the liquid phase which is the abundance desired. This correction is made by relation (2) in which K is the equilibrium constant for equation (3), using molar concentrations in the expression.

$$K = \frac{(\text{B}^{10})_{\text{liquid}} \times (\text{B}^{11})_{\text{gas}}}{(\text{B}^{11})_{\text{liquid}} \times (\text{B}^{10})_{\text{gas}}} = \frac{(\text{B}^{11})_{\text{gas}}}{(\text{B}^{11})_{\text{liquid}}} \div \frac{(\text{B}^{10})_{\text{gas}}}{(\text{B}^{10})_{\text{liquid}}} \quad (2)$$

$$(\text{B}^{11}/\text{B}^{10})_{\text{liquid}} = \frac{(\text{B}^{11}/\text{B}^{10})_{\text{gas}}}{K} \quad (2A)$$

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A second correction must be made for the change in the abundance due to the addition of a finite amount of BF_3 gas.

A calculation of the equilibrium constant K for the isotopic exchange of BF_3 gas with $(\text{CH}_3)_2\text{O}:\text{BF}_3$ was made by McCaulay.⁷ Accepting the value of 1.016 obtained by S.A.M. Laboratories for the simple process fractionation factor at 100°C.:

$$\alpha = \frac{(\text{B}^{11}/\text{B}^{10})_{\text{vapor}}}{(\text{B}^{11}/\text{B}^{10})_{\text{liquid}}} = 1.016,$$

as determined from the distillation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$, and taking the degree of dissociation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ as 60% at that temperature as calculated by McCaulay⁸ from the data of Brown and Adams,⁹ the equilibrium constant K is calculated to be 1.027 at 100°C.

Experimental measurement of this constant showed a value of 1.025 ± 0.002 at 25°C. The experimental and the calculated value may be considered in excellent agreement.

In making the calculations it was assumed that the measurement of fractionation in a packed column whose plates were determined from simple distillation is a valid determination of the true fractionation factor. In the exchange reactions studied by Urey^{10,11} the number of plates was not always found to be a measure of the true fractionation factor. The processes involved in the fractionation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ are less complicated than in the systems studied by Urey, and the assumption is probably valid. Furthermore, the fact that approximately the same fractionation factor has been observed in experiments with different types of packing materials using different calibrating mixtures provides further evidence that the true fractionation factor has been determined.^{1,2}

In making the calculations, it was assumed that the separation is due entirely to chemical exchange in the dissociation process, since it has been observed that the molecule containing the light isotope B^{10} has an apparently lower volatility in the distillation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ and also in the distillation of all other compounds of boron which have been studied.¹

Finally, the assumption has been made in comparing the experimental and the calculated values that both of these values are independent of temperature. The values calculated by McCaulay⁸ for the degree of dissociation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ from the data of Brown and Adams⁹ indicate that the degree of dissociation is reasonably constant, varying from 0.55 at 30°C. to 0.61 at 100°C. If the measured degree of dissociation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ is constant, it appears reasonable to assume that the fractionation which depends on the relative degrees of dissociation of $(\text{CH}_3)_2\text{O}:\text{B}^{10}\text{F}_3$ and $(\text{CH}_3)_2\text{O}:\text{B}^{11}\text{F}_3$ would also be constant. This assumption is in agreement with the report made by the S.A.M. Laboratories¹ that the observed fractionation factor is independent of

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temperature over the range from 60° to 100°C. Although typical values of the equilibrium constants for a number of isotopic exchange reactions calculated from spectroscopic data by Urey and Grieff¹² for 273°K. and 298°K. indicate considerable temperature variations, the assumption that the equilibrium constant K for the isotopic exchange of BF₃ with (CH₃)₂O:BF₃ according to reaction (3) is independent of temperature is probably substantiated by the constancy of the dissociation constant.

The value accepted for the equilibrium constant K for reaction (3) is 1.025, the experimentally determined value. Although it is difficult to make a precise experimental determination, the assumptions involved in obtaining the calculated value while satisfactory in estimating the equilibrium constant, are not definitely enough proven to lead to a better value than the experimental value.

The measurement of the equilibrium constant for the isotopic exchange with BF₃ was carried out by making (CH₃)₂O:BF₃ of 91 atom % B¹⁰ composition and comparing a sample of BF₃ in equilibrium with this (CH₃)₂O:BF₃ with the original BF₃. The determination of the equilibrium constant using the exchange procedure also constitutes a proof of the reliability of the exchange method of preparing the BF₃ mass spectrometer samples. If the equilibrium is rapidly reached, and if the equilibrium constant used in making the calculations is determined by the same method as is used in carrying out the unknown analyses, the method must be valid. Since, in addition the equilibrium constant so determined is in essential agreement with one calculated from entirely independent considerations, the evidence supporting the validity of the procedure is even stronger. The conclusion that the exchange method is more accurate than the original CaF₂ conversion procedure is based primarily on this experiment. An analysis of the (CH₃)₂O:BF₃ made from BF₃ of 91 atom % B¹⁰ composition using the CaF₂ conversion procedure in the analysis was made at the same time and the analysis obtained was found to be slightly low while the analysis obtained using the exchange method has been proven to be correct.

The only potential source of difficulty in the exchange method would be the accidental introduction of impurities. Careful consideration was given to sources of error due to impurities in the two procedures used in preparing mass spectrometer samples. The conclusion was reached that errors due to impurities were more likely in the CaF₂ conversion.

The exchange method for preparing BF₃ samples is now used for all mass spectrometer analyses of the product prepared in this laboratory. This method is, however, used only for the product. The samples taken from various intermediate points in the fractionation unit for control purposes, which range from 10 to 95 atom % B¹⁰, are analysed by the "rapid method"⁴ in which a mass spectrometer is not required. Accurate and rapid mass spectrometer analyses in the 95 atom % B¹⁰ range are thereby made possible by avoiding analyses of samples outside of this range which would cause "memory" effects. For the same reason, all of the analyses made in testing the methods of preparing samples were made in the 95% range.

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Figure 1
Exchange Apparatus

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The BF_3 samples prepared by the exchange procedure are compared with a standard BF_3 sample of 95.32 atom % B^{10} composition. This standard was analysed by Inghram¹³ by the absolute method with a heavy metal mass spectrometer at the S.A.M. Laboratories following the procedure described³ for the absolute determination of the normal isotopic abundances.

The comparison measurements are made by a potentiometric comparison of one ion current against an amplification of the other ion current using the galvanometer as a null instrument instead of by comparison of galvanometer deflections according to the procedure described by Inghram.³ The null method is more rapid and has been shown to be entirely satisfactory for abundances above 90 atom % B^{10} .

The precision obtained in the exchange procedure is $\pm 0.1\%$ for the analysis of 95 atom % B^{10} . This is in agreement with the estimated precision of $\pm 0.1\%$ for the null method used for mass spectrometer comparisons. It is better than the precision of the absolute determination of the standard used for abundance comparisons which is $\pm 0.18\%$ (average deviation).¹³

The experimental work is described below. Although the object of this report is to describe the exchange procedure which has been adopted for routine analyses, and to show the validity of this procedure, it has been necessary to consider in detail the conversion procedure in an attempt to explain the sources of error attributed to the conversion procedure which lead to the observed discrepancies between the two methods of preparing samples. In considering the precision of the exchange method, it has also been necessary to consider the precision of the mass spectrometer measurements used in conjunction with the exchange method of preparing samples.

III. EXPERIMENTAL

A. Exchange Procedure for Preparing BF_3 Samples

The apparatus used to bring the boron trifluoride gas to equilibrium with $(\text{CH}_3)_2\text{O}:\text{BF}_3$ is shown in Figure 1. Bulb (A) is a storage bulb for the 95 atom % B^{10}F_3 prepared when needed by the CaF_2 procedure using the conversion tube (B) and the trap (C) and following the procedure described in section B. Bulb (D) is the vessel used for bringing the liquid $(\text{CH}_3)_2\text{O}:\text{BF}_3$ to be analysed to equilibrium with a sample of BF_3 gas.

Two ml. of the liquid to be analysed are added with a pipet through the ground joint in bulb (D). The bulb is attached to the vacuum manifold, the liquid is frozen by immersing in a dry ice-trichlorethylene mixture, and the bulb is evacuated. Bulb (E) and tube (G) are evacuated at the same time. The $(\text{CH}_3)_2\text{O}:\text{BF}_3$ may be melted, refrozen, and evacuated again, but this is not ordinarily necessary for samples taken from a distillation unit which should not contain volatile impurities.

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A sample of BF_3 gas of known isotopic composition from bulb (A) is transferred to the evacuated bulb at (E) by application of liquid nitrogen to bulb (E). The number of mols of gas taken is determined by measuring the pressure in bulb (E) at room temperature using a closed mercury manometer at (F), the volume of bulb (E) including the manifold having been previously measured. The gas in (E) is transferred to the reaction bulb (D) by condensing with liquid nitrogen.

The bulb (D) is then removed from the manifold with its attached stopcock and shaken for one minute to allow the system to come to equilibrium. The BF_3 is then condensed on the walls of the bulb with liquid nitrogen, and the shaking continued for an additional minute after melting the solids formed. In this way any possible difficulty due to slow diffusion of the BF_3 in the upper part of the bulb (D) is eliminated. Although no attempt has been made to show that this step is necessary, it seems a worthwhile precaution. During the shaking, bulb (E) is again evacuated.

To remove the sample of BF_3 gas, the bulb (D) is attached to the manifold and the system evacuated above the stopcock on bulb (D). The gas is then transferred rapidly back into the evacuated bulb (E) by applying liquid nitrogen to bulb (E). The stopcock of bulb (D) is closed as soon as the gas is condensed in bulb (E) minimizing distillation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ and other less volatile compounds. Dry ice-trichlorethylene is applied to bulb (E) to keep any less volatile compounds condensed and the BF_3 is allowed to expand. When equilibrium pressure is reached the gas is again transferred rapidly using liquid nitrogen into the evacuated sample tube (G) which can be fitted to the manifold of the mass spectrometer. The stopcock to bulb (E) is closed as soon as the gas is condensed in tube (G).

The gas is allowed to expand into the manifold and the pressure measured. If the pressure is such that on condensing all of the gas into tube (G) the pressure will be greater than one atmosphere, then part of the gas is pumped out. If the $(\text{CH}_3)_2\text{O}:\text{BF}_3$ contains impurities, a considerable part of the BF_3 gas may be used up by reacting with the impurities. The amount of gas recovered will then be small enough that no excess gas will have to be pumped off.

The gas is then frozen in tube (G) with liquid nitrogen and evacuated until no discharge is obtained with a spark coil. The frozen BF_3 is melted, refrozen, and evacuated a second time. The sample tube (G) may then be removed and attached to the manifold of the mass spectrometer.

A mercury diffusion pump backed by a Cenco Hyvac mechanical pump is used for evacuation. Except during the last step in which tube (G) is evacuated, a high vacuum is not necessary and pumping a short time with the mechanical pump produces a satisfactory vacuum. Capillary tubing has been used to minimize the volume of the manifold. Extra ground joints are provided on tube (G) and bulb (E) which are used for opening these parts for cleaning. The volume of the sample tube (G) is about 10 ml. and the volume of bulb (D) is 50 ml. Bulb (D) would ideally be constructed in the shape used by Hutchison⁶ but a spherical bulb is satisfactory.

The volume of (E) was measured by comparison of the pressure of a quantity of air with that in a known volume and was found to be 40 ml. The gas is usually added to fill this volume to a pressure of about 600 mm. of mercury, the actual pressure being measured. Assuming a temperature of 25°C., 600 mm. corresponds to 1.29 milli-mols as compared with 21.7 milli-mols of liquid taken in 2.00 ml. of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ with a density of 1.23. The mol ratio gas/liquid is thus 0.059.

Care must be taken to prevent errors due to the presence of impurities in the system resulting from hydrolysis of previous samples or from reaction of BF_3 with stopcock grease. The bulb (D) and its accompanying stopcock are cleaned, washed with acetone, and dried by evacuation after each use. The gas is removed from the sample tube (G) by evacuation immediately after analysis to minimize reaction of BF_3 with the stopcock grease. This tube need be cleaned only occasionally. The whole system must be cleaned occasionally, regreasing all stopcocks with Apiezon M. From time to time it is necessary to completely dismantle the apparatus and clean or replace the tubing.

B. Calculations for Analyses Using Exchange Procedure

The atom ratio $\text{B}^{11}\text{F}_3/\text{B}^{10}\text{F}_3$ in the gas sample is measured directly with the mass spectrometer. The atom ratio $\text{B}^{11}/\text{B}^{10}$ for the liquid phase in equilibrium with this gas can be calculated from the equilibrium constant of reaction (3). According to equation (2):

$$K = \frac{(\text{B}^{11})_{\text{gas}}/(\text{B}^{10})_{\text{gas}}}{(\text{B}^{11})_{\text{liquid}}/(\text{B}^{10})_{\text{liquid}}} \quad (2)$$

From the isotope ratio in the liquid phase, the atom % in the liquid phase is calculated by equation (5).

$$\text{atom \% B}^{11} = \frac{\text{B}^{11}}{\text{B}^{10} + \text{B}^{11}} \cdot 100 = \frac{(\text{B}^{11}/\text{B}^{10})}{1 + (\text{B}^{11}/\text{B}^{10})} \cdot 100 \quad (5)$$

This result must then be corrected for the change in concentration caused by the addition of gas of known concentration.

If the atom ratio $\text{B}^{11}/\text{B}^{10}$ in the original liquid = x (the unknown),

the ratio $\text{B}^{11}/\text{B}^{10}$ in the original gas = y,

the ratio $\text{B}^{11}/\text{B}^{10}$ in the resulting gas = z,

the ratio $\text{B}^{11}/\text{B}^{10}$ in the resulting liquid = w = z/K,

and the mol ratio gas/liquid = A,

then the atom % B^{11} in the original liquid is:

$$\text{atom \% B}^{11} = \left(\frac{x}{1+x} \right) 100 = \left[\left(\frac{z}{1+z} - \frac{y}{1+y} \right) A + \frac{(z/K)}{1+(z/K)} \right] 100 \quad (6)$$

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Figure 2

CaF₂ Conversion Apparatus

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Equation (6) expresses the correction made in the observed abundance for the equilibrium constant as well as for the amount of gas added. When A , z , y , and $(z-y)$ are small, the correction term may be expressed by an approximation:

$$A \left(\frac{z}{1+z} - \frac{y}{1+y} \right) \approx A(z-y) \quad (7)$$

The calculations have been simplified by the use of the ratio B^{11}/B^{10} , which is small when dealing with high concentrations of B^{10} . When the final corrected value of atom % B^{11} is obtained this is converted into atom % B^{10} , which is the value generally reported.

C. CaF_2 Conversion Procedure for Preparing BF_3 Samples

The procedure used is essentially that developed by the S.A.M. Laboratories.¹ The form of apparatus used in this laboratory during the past year is shown in Figure 2.

The incubation tube (A) consists of a 15 cm. length of 20 mm. pyrex tubing with a length of 12 mm. tubing attached at the neck. In this tube 6 grams of C.P. CaF_2 are placed with 3 ml. (3.7 grams) of $(\text{CH}_3)_2\text{O}:\text{BF}_3$ and the mixture stirred thoroughly with a monel rod. This tube is then heated in an electric oven for at least 8 hours at 70°C . to remove the $(\text{CH}_3)_2\text{O}$ quantitatively and convert the $(\text{CH}_3)_2\text{O}:\text{BF}_3$ to $\text{CaF}_2:\text{BF}_3$. This tube is then sealed to the vacuum manifold in the position shown in Figure 2. An electric heater surrounding the tube (A) and regulated with a variac transformer is used to further increase the temperature in the tube. The temperature is measured with an iron-constantan thermocouple. One junction is placed next to the glass within the cylindrical opening in the heater. The second junction is placed in ice water and the temperature difference is measured by potential difference as determined with a potentiometer. After testing the system for vacuum with a discharge coil, the temperature is gradually increased while pumping the system with a mercury vapor diffusion pump backed with a Cenco Hyvac mechanical pump. The temperature is increased to about 120°C . and held for 10 minutes at that point. The stopcock to the pump is then closed and the trap (C) surrounded with ice water. The temperature is then further increased and the 500 ml. storage bulb (B) is filled to a pressure of 500 mm. of mercury as measured on a closed mercury manometer at (D). This amount corresponds to a recovery of approximately 40% of the BF_3 present. The stopcock to the trap (C) is then closed and the heater removed. The gas in bulb (B) is condensed with liquid nitrogen, pumped until a high vacuum is obtained, and allowed to vaporize in the bulb.

The sample system at (E) consists of a set of five sample tubes, two of which are shown. Each of these consists of a 20 cm. length of 12 mm. tubing with a break seal at one end, sealed off at the other end, and attached to the manifold by an 8 mm. side-arm tube. Enough gas is allowed to expand into the sample tubes so that one tube will be filled to a pressure of $1\frac{1}{2}$ atmospheres. This gas is condensed into the first tube with liquid nitrogen and pumped again to a high vacuum. This tube is then sealed off and used for mass spectrometer

analysis removing the sample through the break seal. It was the practice generally when this apparatus was used to fill two or three of these sample tubes, saving the extra ones in reserve. The drying tube at (F) contains CaCl_2 and is used to keep moisture out of the system during the glass blowing required to seal on the sample tubes at (E) before making the conversion, and to seal on the incubation tube at (A) during the conversion.

To prepare the system for the next sample, the tube is removed from (A) and the trap (C) and the tubing between (A) and (C) are washed with distilled water and dried with a stream of air. The used sample tubes are replaced and the new sample tubes at (E) are tested for leaks.

The calcium fluoride used was an Eimer and Amend product supplied by S.A.M. Laboratories as the best available reagent for the purpose. The reagent was used without drying.

D. Mass Spectrometer Analyses of Boron Using Null Method

In the usual method of measuring relative abundances of the boron isotopes,³ the maxima of positive ion current collected at a single point at different accelerating potentials are compared. The mass spectrometer designed and constructed by Inghram³ has an additional collector plate so situated that current corresponding to both mass numbers 10 and 11 may be collected simultaneously.

This second method of determining isotope abundance uses a portion of the ion current from mass 10 which is collected on this feed back collector plate to cancel or nullify the current from mass 11 which is collected on the FP-54 electrometer plate. Both ion currents are passed through high resistances and the relative potential drops produced are measured. That from the feed back input resistor is amplified by the feed back amplifier and causes a current to flow through a constant resistance decade to ground. The portion of the resulting potential needed to counterbalance that developed by the mass 11 current flowing through the input resistor of the FP-54 electrometer is determined by varying the decade setting until no deflection is observed with the galvanometer.

The details of the manipulation of the mass spectrometer controls for the null method are to be described in a report to be issued.¹⁴

When the decade readings have been obtained for both standard and sample the absolute atom ratio B^{11}/B^{10} is calculated from the absolute atom ratio of the standard by equation (8):

$$(B^{11}/B^{10})_{st} \cdot \frac{R_x}{R_{st}} = (B^{11}/B^{10})_x \quad (8)$$

where R = decade reading,
x refers to unknown, and
s refers to standard.

The proportional relationship of decade resistances to atom ratios is derived from the fact that the amount of B^{10} potential which must be used to nullify that due to B^{11} is proportional to the atom ratio B^{11}/B^{10} and also to the observed decade resistance. A number of assumptions are involved in using this proportional relationship, but the errors introduced are not serious.¹⁵

E. Approach to Equilibrium in Exchange Procedure

Using 84.8 atom % $B^{10}F_3$ gas with $(CH_3)_2O:BF_3$ of approximately 95 atom % B^{10} , and varying the time of shaking, an attempt was made to measure the rate at which equilibrium is approached. Very little difference could be detected between samples shaken for 10 minutes and samples shaken for 5 seconds. Except for the experiments for very short time intervals the gas was condensed down once in the middle of the experiment as in the routine procedure described in section A.

In order to contact the gas with the liquid for very short times a modified procedure was used. The gas was admitted to the bulb (D) (Figure 1) containing $(CH_3)_2O:BF_3$ at room temperature, at the same time applying liquid nitrogen to the bulb. As soon as the BF_3 had condensed in the bulb, but before the $(CH_3)_2O:BF_3$ had been frozen, the stopcock was closed, the liquid nitrogen removed from around the bulb, and the bulb removed from the vacuum manifold. The BF_3 was quickly evaporated by applying warm water to the outside of the bulb and the bulb shaken for the specified time. The bulb was then immediately immersed in liquid nitrogen and kept there while it was quickly attached to the manifold. The stopcocks were opened and the BF_3 distilled into bulb (E) by applying liquid nitrogen to bulb (E) and removing the liquid nitrogen from bulb (D).

An experiment was also carried out in which 84.8 atom % $B^{10}F_3$ was contacted with $(CH_3)_2O:BF_3$ of approximately 95 atom % B^{10} without shaking. This was the only experiment in which a large deviation from equilibrium was observed. The gas was simply added in the usual manner and allowed to stand for the specified time in the bulb (D) and the vacuum manifold, and then pumped off.

F. Measurement of the Equilibrium Constant for Isotopic Exchange of BF_3 with $(CH_3)_2O:BF_3$

McCauley⁷ has described in detail the apparatus and procedure by which 5 ml. of $(CH_3)_2O:BF_3$ were made from $(CH_3)_2O$ and BF_3 gas of 91 atom % B^{10} composition, saving a sample of gas for comparison with the mass spectrometer. This $(CH_3)_2O:BF_3$ was brought to equilibrium with a sample of the same gas used in making the $(CH_3)_2O:BF_3$ following the routine procedure for the exchange method described above except that twenty minutes were allowed for equilibrium to be reached. The gas obtained was compared with the original gas using the mass spectrometer. It was not found possible to obtain the precision required by the null method generally used for routine analyses. The deflection method described by Inghram³ was therefore used since the effects of drift in the electronic system are smaller in the deflection method. A measurement was made of one gas sample between two measurements of the second gas sample. The experiment was repeated using the two samples in reversed order. The average of five galvanometer deflections was taken for each measurement.

G. Comparison of the Two Procedures for Preparation of BF₃ Samples

Samples of BF₃ gas were prepared by the exchange method and by the CaF₂ conversion method from the same (CH₃)₂O:BF₃. The procedure used for analysis of these samples was the following. First a standard was measured, then the first unknown gas, the second unknown gas, the first unknown gas again, and finally the standard again. Interpolated values of the standard and the first unknown sample are compared with the value for the second unknown sample assuming a drift in the instrument which is linear with time.

Boron fluoride gas samples having B¹⁰ abundances both higher and lower than the (CH₃)₂O:BF₃ being analysed were used in the exchange method in order to check the attainment of equilibrium in these experiments.

IV. RESULTS

A. Approach to Equilibrium in Exchange Procedure

The data obtained in the experiments on the approach to equilibrium are shown in Table I. Analyses are expressed in terms of atom % B¹⁰.

TABLE I

Approach to Equilibrium

<u>Time of Contact</u>	<u>Initial Gas</u>	<u>Analysis</u>	<u>Difference From Equil.</u>
A. Sample D-767			
10 min.	84.8%	96.1%	+0.1%
2 min.	84.8	95.9	-0.1
30 sec.	84.8	96.0	0.0
5 sec.	84.8	95.7	-0.3
5 min.	96.4	95.9	-0.1
	Equilibrium Value	96.0	
B. Sample E-64			
2 min.	84.8	96.3	0.0
30 sec.	84.8	96.3	0.0
35 sec.*	84.8	92.5	-3.8
	Equilibrium Value	96.3	

* (This sample was not shaken. All other samples were shaken)

The experiments with sample D-767 showed that the period of shaking did not affect the equilibrium reached using 84.8% initial gas if the period was 30 seconds or longer. For 5 seconds, a slightly low value was obtained. One experiment using 96.4% initial gas was in agreement with the average value from experiments with 84.8% gas leading to the conclusion that the same equilibrium can be reached using initial gas of either a higher or a lower B^{10} concentration. Further experiments with gas of a higher and lower concentration verifying this conclusion are shown in Table II, samples D-388, D-408, and D-410. The period of shaking in these latter cases was 2 minutes or more.

The experiments with sample E-64 showed that without shaking equilibrium is slowly attained, only 67% of the theoretical exchange being observed in 35 seconds.

The conclusion may be drawn that when the initial B^{10} abundance of the BF_3 gas is near to that of the $(CH_3)_2O:BF_3$, a two minute period is more than sufficient for equilibrium conditions to be established within 0.1% which is within the limits of error of the mass spectrometer. Further experiments would be required to establish the time necessary for equilibrium to be reached starting with normal BF_3 (18.8 atom % B^{10}). Because of the relatively large correction which is necessitated for the amount of B^{11} introduced by the use of normal BF_3 , the procedure using normal BF_3 has not been investigated.

B. Measurement of Equilibrium Constant for Isotopic Exchange

The existence of a rapidly attainable equilibrium having been established, the acceptance of the exchange method for preparing samples depends only on an experimental determination of the equilibrium constant for equation (3). The value 1.027 calculated by McCaulay from the accepted value 1.016 for the fractionation factor, α , has been used in the calculations in this report. The value obtained experimentally, 1.025, has been adopted for future applications of the exchange method.

The values obtained from the two experiments described in the experimental section are:

$$\begin{aligned} 1.0264 \pm 0.005 \\ 1.0232 \pm 0.001 \end{aligned}$$

The average obtained from these two values is 1.025 ± 0.001 . A statistically weighted average is 1.023 ± 0.002 to include both of these values.

The measure of error is in each case the statistically calculated probable error. The probable errors of the two experimental values were calculated from the observed deviations in the galvanometer readings in accordance with the accepted statistical methods of computing probable errors of a function from the probable errors of the variables in the function.¹⁶ The probable error of the unweighted average was calculated from the two individual values of K without regard to the estimated errors of the individual values. The probable error of the weighted average was calculated from the

TABLE II

Exchange and Conversion Procedures

<u>Sample</u>	<u>Exchange Analysis</u>			<u>Conversion Analysis</u>		<u>Difference</u>
	<u>Sample</u>	<u>Gas Used</u>	<u>Analysis</u>	<u>Sample</u>	<u>Analysis</u>	
D-386		96.6%	95.7%		95.6%	-0.1%
D-388	A	96.6	95.6	C	95.4	
	B	92.3	95.8	C	95.3	
	avg.		95.7 ± 0.1		95.4 ± 0.1	-0.3
D-408	A	96.6	95.7	D	95.5	
	B	96.6	96.0	D	95.5	
	C	92.3	95.7	D	95.5	
	avg.		95.8 ± 0.1		95.5 ± 0.1	-0.3
D-410	A	96.6	95.7	D	95.4	
	B	96.6	95.7	D	95.3	
	C	92.3	95.5	E	95.4	
	avg.		95.6 ± 0.1		95.4 ± 0.1	-0.2
D-550		94.3	95.6		95.2	-0.4
D-551		94.3	95.6		95.1	-0.5
D-633		95.0	96.1		95.7	-0.4
D-635		95.0	95.3		95.0	-0.3
Equil. Const.		91.5	91.5		91.0	-0.5
					avg. =	-0.3

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errors calculated for the individual determinations in accordance with the approved statistical methods.¹⁶ Since the probable error is defined statistically as the error such that there is a 50% chance that the error will be greater than the probable error, allowance must be made for possible errors somewhat greater than 0.002. More than two determinations would be required to accurately determine the error of the determination.

The precision obtained in this experiment is much greater than needed. If the error is five times the calculated probable error, that is if the constant were 1.025 ± 0.010 , the concentration of B^{10} in a liquid sample in equilibrium with gas of 95.00 atom % B^{10} concentration would be 95.12 ± 0.05 atom % B^{10} . Yet the absolute determination of the standard used gave a value of 0.047 ± 0.002 for B^{11}/B^{10} which is 95.52 ± 0.18 atom % B^{10} expressing the error in this case by the average deviation.¹³ Under these circumstances the error due to the uncertainty in the equilibrium constant is much less than the error due to uncertainty in the absolute determination of the standard and is generally less than the uncertainty of routine comparisons carried out by the null method since the errors of the null method are generally greater than the errors in the above experiment as will be shown in section E.

C. Comparison of the Two Procedures for Preparation of BF_3 Samples

The data obtained in eight experiments comparing the exchange and CaF_2 conversion methods for preparing mass spectrometer samples are presented in Table II. For samples of $(CH_3)_2O:BF_3$ numbered D-388, 408, and 410 more than one comparison was made. The gas samples prepared from these samples are designated in the table by letters. Samples on the same line in the table were compared with each other. The average values and the average deviations have been calculated and the difference between the two methods tabulated. The average difference is $0.3\% \pm 0.1\%$ (average deviation). From the three experiments in which more than one determination was made the conclusion may be drawn that the precision of the comparison is $\pm 0.1\%$ (average deviation). A definite error is therefore present.

In the experiment in which the equilibrium constant for reaction (3) was measured, $(CH_3)_2O:BF_3$ of known isotopic abundance was prepared from analysed BF_3 . A sample of this $(CH_3)_2O:BF_3$ was analysed using the CaF_2 conversion procedure. Comparison with the analyses using the exchange procedure which were obtained in the course of the equilibrium constant determination showed the CaF_2 conversion to be too low by 0.5%. The data are shown in the last entry in Table III.

The concentration of the initial gas is given in all cases so that the data may be used to show the agreement obtained with high and low initial gas concentrations. For samples D-408 and D-410 the analyses obtained using high initial gas were relatively high and for samples D-388 and D-767 (Table I), the analyses using high initial gas were relatively low. The differences are small, however, and no significant trend is indicated.

D. Precision of Mass Spectrometer Using Direct Deflection Method

Inghram³ reported the precision of the mass spectrometer as 0.2% of the ratio B^{11}/B^{10} which is less than 0.02% in the region between 90 and 100% B^{10} . As indicated below, measurements made in this laboratory are essentially in agreement with this estimate.

The data previously presented for the precision of the determination of the equilibrium constant K of equation (3) may be used as a measure of the precision of the mass spectrometer measurements in which the ratio of the galvanometer deflections are measured directly. Accepting the concentration of the liquid phase in the equilibrium constant experiment as 91.50 atom % B^{10} as determined by comparison with the absolute standard, the concentrations of the gas phase are:

$$\begin{aligned} 91.28 \pm 0.05 \text{ atom \% } B^{10} \\ 91.31 \pm 0.01 \text{ atom \% } B^{10} \end{aligned}$$

The weighted average is $91.31 \pm 0.01\%$ and the unweighted average is $91.30 \pm 0.02\%$.

The data from another experiment in which a secondary BF_3 gas standard was compared with the primary standard should be considered. This comparison was made by the same procedure as was described for the mass spectrometer comparison of the two gas samples in the equilibrium constant experiment. The values obtained were:

$$\begin{aligned} 94.22 \pm 0.05 \text{ atom \% } B^{10} \\ 94.31 \pm 0.04 \text{ atom \% } B^{10} \end{aligned}$$

The weighted average is $94.25 \pm 0.03\%$ and the unweighted average is $94.26 \pm 0.05\%$.

Thus, Inghram's estimate of the precision may be considered valid when all possible precautions are taken.

Neither of the methods of preparing BF_3 samples has been shown to be accurate to 0.02%. The preparation of the BF_3 samples was studied only with the null method of analysis. The limiting error in routine determinations has been shown in section B to be the determination of the abundance of the absolute standard. For this reason the higher precision of the direct deflection method cannot be used to improve the accuracy of the analysis. There has been, therefore, no necessity for studying the precision of the exchange method of preparing samples with the direct deflection method.

The direct deflection method carried to its ultimate limit of accuracy is required only for the determination of small separation factors as in the equilibrium constant determination described in this report. The direct deflection method has also been used for analyses of samples with an abundance less than 90 atom % B^{10} because of the doubtful applicability of the null method.

E. Precision of Mass Spectrometer Using Null Method

When the null method for mass spectrometer determinations was first introduced, a set of samples were compared by both the deflection and null methods. Agreement was established to 0.1%. The values are recorded in Table III.

TABLE III

Agreement of Deflection and Null Methods

	<u>Atom % B¹⁰</u>				
	<u>Null Method</u>				
<u>Sample</u>	<u>1st Meas.</u>	<u>2nd Meas.</u>	<u>avg.</u>	<u>Defl. Method</u>	<u>Difference</u>
C-384	94.83	94.92	94.88	94.77	+0.11
C-404	94.95	94.77	94.86	94.79	+0.07
C-423	95.31			95.19	+0.12
C-424	95.00			95.01	-0.01
Average					+0.07

It is not possible to test the precision of the null method by calculating deviations in the individual readings **as the reading accepted** is the final rather than the average value of a series of readings. The best test of the precision is the data in Table IV showing typical measurements of the drift in the decade reading for the standard sample.

TABLE IV

Drift in Decade Reading for Standard

<u>Expt.</u>	<u>Standard</u>	<u>First Unknown</u>	<u>Second Unknown</u>	<u>Standard</u>	<u>% Change Standard</u>	<u>% Change B¹⁰ Conc.</u>
1	280	220	205	270	-3.7%	-0.19%
2	275	210	200	270	-1.9	-0.10
3	300	215	265	290	-3.3	-0.17
4	300	222	185	280	-6.7	-0.34
5	275	200	203	255	-7.7	-0.39
6	257	205	300	260	+1.2	+0.06

Since two samples are generally measured with each pair of standards, the data for drift are shown for cases where two unknowns were measured together. A standard was measured, then two different unknown, then the same standard was repeated. From the decade readings for the standard sample, the relative change in the standard was calculated and the absolute error in the atom % B¹⁰ calculated from this for an analysis of an unknown of 95 atom % B¹⁰. From these data the maximum error of the average is found to be ± 0.2 atom % B¹⁰. Since the drift is at least partly taken account of in the averaging process, the

error can be safely set at less than 0.1%, although a more accurate estimate of the limiting precision of the method could only be made from the comparison of duplicate determinations by the null method of a considerable number of samples. The data for such a calculation are not available. The precision definitely does not appear to be as good as that obtainable with the direct deflection method (0.02%) in which the electronic circuit involved is simpler.

The null method was found to be reliable for analyses of samples between 90 and 100 atom % B^{10} . It should not be used for less concentrated samples since a part of the B^{11} beam is collected along with the B^{10} on the feed back collector and a variable error is thus introduced. The amount collected can be neglected when the abundance of B^{11} is less than 10%.

The conclusion reached is that for the routine analysis of $(CH_3)_2O:BF_3$ containing 95 atom % B^{10} the precision of the exchange method of preparing BF_3 samples and of the null method mass spectrometer determination itself are each within 0.1%, and that the precision of the procedure using these two methods is better than the accuracy with which the absolute standard is known, which is 0.2%.¹³

F. Evaluation of CaF_2 Conversion Procedure

As shown in Table II excellent precision can be obtained in calcium fluoride conversions carried out under reproducible conditions. Experiments carried out in a newly constructed apparatus failed to show any significant difference from those carried out in an apparatus which had been in constant use for over a year indicating that the contamination of the vacuum line with hydrolysis products of BF_3 is not a serious source of error. Further experiments were therefore carried out in an attempt to find the cause of the 0.3% discrepancy between the conversion and exchange procedures.

An experiment in which a sample of $(CH_3)_2O:BF_3$ containing added water was compared with a sample containing no added water indicated a difference of 0.3% which was attributed to the dilution effect of the 18.8% B^{10} removed from pyrex glass by the HF formed. The analysis without water was 95.2 atom % B^{10} and with water 94.9%.

Following the theory that attack of the glass is probably the major source of error, two types of experiments were tried. First the BF_3 was condensed with liquid nitrogen in the trap as soon as it was liberated, in an attempt to decrease any gas phase reaction with the hot incubation tube. The results did not differ from those obtained by the usual procedure. Since the gas liberated was condensed in this modification of the procedure, the rate of liberation of BF_3 was followed by the temperature of the tube instead of by the pressure in the system. The temperature required for complete evolution under given conditions can be determined by observing the temperature during the course of an experiment following the usual procedure. Although it was not possible to prove a necessity for this freezing down procedure, it does no harm in any case, and may offer some improvement.

Consideration was also given to the possibility that the attack on the glass could take place during the incubation period. An incubation tube constructed of copper and attached to the vacuum line with a brass coupling and copper-glass seal was tried. The copper tube was constructed by pinching the end of a piece of copper tubing and silver soldering the closed end. No evidence was obtained to show that any different result was obtained with this modification.

Thus, neither of these experiments has proved that the source of error in the conversion procedure is a reaction with the glass. The proof that the CaF_2 conversion is in error must rest mainly on the fact that erroneous results were obtained in the experiment using known $(\text{CH}_3)_2\text{O}:\text{BF}_3$ made from analysed BF_3 . Although it has not been possible to demonstrate the exact source of error in the CaF_2 procedure, there are a number of considerations which lead to the conclusion that the CaF_2 conversion has more potential sources of error than the exchange method for preparing samples.

The fact that only 40% of the theoretical amount of boron is converted to BF_3 in the routine procedure is one possible source of error. It is not unreasonable to assume that there is an isotopic fractionation in the process of dissociation (9):

If the isotopic fractionation takes place in the same manner as all other reactions of boron compounds which have been studied, the gas will be enriched in B^{11} . But experimentally the gas is found to have too much B^{10} . Instead of accounting for the observed discrepancy between the conversion and exchange procedures, this factor adds to the discrepancy.

In order to estimate the magnitude of this additional discrepancy the equilibrium constant for reaction (10):

is assumed to be of the same order of magnitude as that for the reaction (3), that is about 1.027. Using the Rayleigh equation for the distillation of 40% to the vapor phase with an equilibrium constant of 1.027, if the initial concentration is 95.00 atom % B^{10} , the gas taken off will be 95.11 atom % B^{10} . In this case a correction of 0.1% for this fractionation would be applied to all determinations made in the 95% range by the CaF_2 conversion method. Making such a correction, the discrepancy between the two methods would be increased from 0.3% to 0.4%.

Thus, the error due to fractionation in the dissociation of $\text{CaF}_2:\text{BF}_3$ is not serious in routine determinations. Furthermore, it could be reduced to a negligible factor by modifying the procedure to obtain 80-90% yields of gas, according to the method described by Kirshenbaum.¹

The error presumably must then be introduced by reaction with glass or with boron compounds in the vacuum system. The fact that the CaF_2 conversion involves longer contact with the apparatus, higher temperatures, and consequently more opportunity for reaction with glass, for reaction with water and for thermal decomposition than the exchange procedure, leads to the conclusion that errors of this sort are more likely to arise in this procedure than in the exchange procedure.

The CaF_2 procedure seems to offer no advantage over the exchange procedure for the routine work of this laboratory where all mass spectrometer samples are in the same range. Since the exchange method as described requires initial gas of approximately the same concentration as the $(\text{CH}_3)_2\text{O}:\text{BF}_3$ to be analysed, it would be desirable if only occasional analyses were being made to use the CaF_2 conversion or to develop an exchange procedure using normal (18.8% B^{10}) BF_3 .

For some purposes the procedure as described in this report would be satisfactory. In fact the procedure could even be simplified. The use of break seals is an unnecessary part of the procedure. In fact if the mass spectrometer analysis is to be made immediately, the use of break seals is probably undesirable. It is also likely that a procedure could be developed to avoid the eight hour incubation. Experiments which have been carried out indicate that when the incubation period is shortened a mass spectrometer peak due to C^{12} is observed which interferes with the B^{11} peak. A shorter incubation would have to be carried out under different conditions, probably at a higher temperature.

It is also probable that the CaF_2 conversion procedure could be developed in a more accurate form to eliminate the errors which have caused the discrepancies. The metal incubation tube should be incorporated into this procedure. Care would have to be taken to eliminate contamination from the boron generally present in silver solder if silver solder is to be used in the construction of the tube. It would not be difficult to remove stopcocks completely and to use all clean glass for each run. After removing all of the $(\text{CH}_3)_2\text{O}$ the entire apparatus could then be thoroughly flamed to remove decomposition products. The tube should then be heated until as nearly as possible 100% of the BF_3 is driven off. The BF_3 should be continuously frozen down in the trap with liquid nitrogen. When finished dry ice should be placed around the trap and the BF_3 removed.

G. Evaluation of Exchange Procedure

The precision of the procedure may be estimated from the analyses of duplicate samples prepared by this procedure. The data in Table II may be used for this purpose. The average deviations recorded for the duplicate samples by the exchange procedure (left column of Table II) should be compared with the deviations (right column) for separate analyses of the same sample of gas. The conclusion may be drawn that the precision of the exchange procedure is as good as that of the null method mass spectrometer determination, that is average deviations of about 0.1% may be expected in the range of 95 atom % B^{10} . These conclusions agree with those drawn from the experiments in which the approach to equilibrium and the value of the exchange equilibrium constant were determined.

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Some consideration has been given to the possibility of using this method with normal abundance BF_3 (18.8% B^{10}) as the initial gas. With the gas/liquid mol ratio as now used, this would require a correction of about 4.5% in the analysis of 95 atom % B^{10} . For 0.1% accuracy in the abundance this would require measurement of pressure, volume, and absolute temperature to 2% which is feasible. If the time of equilibrium were found to be reasonable for the use of normal abundance BF_3 , as appears probable, the method would be entirely feasible although for the best possible analyses in the 95 atom % range, it appears that the use of an initial gas nearly in equilibrium with the $(\text{CH}_3)_2\text{O}:\text{BF}_3$ to be analysed is called for.

Further applications of the method have been considered. For the determination of the isotopic fractionation of oxygen, carbon, and hydrogen occurring on distillation of $(\text{CH}_3)_2\text{O}:\text{BF}_3$, samples of $(\text{CH}_3)_2\text{O}$ in isotopic equilibrium could probably be obtained by exchange of $(\text{CH}_3)_2\text{O}$. Other addition compounds of BF_3 could in many cases be analysed by exchange of free BF_3 . Even boron compounds other than addition compounds of BF_3 may come to isotopic equilibrium with BF_3 . Most of these, however, react chemically with BF_3 to form compounds which do not dissociate appreciably to give BF_3 . Such compounds cannot be analysed by exchange with BF_3 . Exchange with $\text{B}(\text{OCH}_3)_3$ might offer a possible method of preparing mass spectrometer samples for boron analyses where BF_3 exchange is not suitable. In all of these reactions, it would be necessary to establish the attainment of a rapid equilibrium for each individual reaction and to determine the isotopic exchange equilibrium constant for the reaction before attempting to use the method for accurate analyses. The type reaction is represented by:

The compound A may or may not contain boron and is any compound which comes to isotopic equilibrium with BF_3 , not necessarily by forming an addition compound. If it should become desirable to carry out an investigation to find whether the process now in use^{1,2} for the separation of boron isotopes is the best possible process, measurements of the exchange equilibrium constants carried out by the procedure described in this report for process (3) might be a convenient method of attack. Measurements of the equilibrium constants for similar reactions for other ethers for which the degree of dissociation of the complex with BF_3 is known would be of particular interest.

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