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AN INTERPRETATION OF THE ISOTOPIC SEPARATION
IN THE DISTILLATION OF METHYL ETHER-BORON FLUORIDE COMPLEX

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AN INTERPRETATION OF THE ISOTOPIC SEPARATION
IN THE DISTILLATION OF METHYL ETHER-BORON FLUORIDE COMPLEX

SUMMARY

In order to calculate an isotopic separation factor for the equation,

which represents the equilibrium occurring in one stage of a new rapid method for B^{10} analysis, it was necessary to consider the mechanism by which isotopic fractionation occurred in the distillation of the methyl ether-boron fluoride complex.

In view of the fact that the B^{11} isotope has been shown to be more volatile than the B^{10} isotope in all distillations of boron compounds in which isotopic separation was observed, it was postulated that separation is due to a chemical exchange reaction and that the difference in vapor pressures between the isotopic compounds is negligible.

Expressions were set up for the equilibrium constant K of the above reaction which, when combined with similar expressions for the one plate fractionation factor α , led to the expression,

$$K = 1 + \frac{\alpha - 1}{\text{Fraction Dissociated}},$$

from which K is calculated to be 1.027 when $\alpha = 1.016$.

These assumptions were substantiated by laboratory experiments which showed an extremely small difference in boiling points between B_{10} complex and B_{11} complex, and which indicated a value of $K = 1.025 \pm .002$.

The value $K = 1.027$ was, therefore, accepted as the desired factor for correcting rapid B^{10} analyses.

INTRODUCTION

The question of interpreting the isotopic fractionation in the distillation of the methyl ether-boron fluoride complex arose when an attempt was made to calculate a correction factor to be applied in a new rapid method for B^{10} analyses¹. In this method a measured amount of methyl ether-boron fluoride complex of unknown B^{10} composition is shaken with a measured amount of boron fluoride gas of known B^{10} content. After equilibrium has been reached, a sample of the gas is withdrawn and its B^{10} content is determined by mass spectrometer analysis. The B^{10} analysis so obtained is equal to the unknown B^{10} content of the methyl ether-boron fluoride complex after a few small corrections are made. One of the necessary corrections is the compensation for a one plate isotopic fractionation represented by the equation,

which may occur between the gas and the liquid. In order to make this correction it is necessary to know the equilibrium constant for the above reaction. Since the one plate fractionation factor α is known for the distillation of methyl ether-boron fluoride complex, it was believed possible to calculate the desired equilibrium constant from the fractionation factor if the mechanism of the distillation were sufficiently well understood. Therefore the task of postulating a mechanism for isotopic separation in the distillation of complex was undertaken.

PROPOSED INTERPRETATION

In all cases in which isotopic separation was observed in the distillation of boron compounds², the heavier isotope, B^{11} , was found to be more volatile than the lighter isotope, B^{10} . In particular this was noted in the distillation of boron fluoride, methyl borate, methyl borate-boron fluoride complex, methyl ether-boron fluoride complex, ethyl ether-boron fluoride complex, and ethyl borate-boron fluoride complex, in which compounds the one plate separation factors ranged from 1.001 to 1.016.

This surprising phenomenon of the lighter compound being less volatile than the heavier compound is contrary to experience in the distillation of binary mixtures of structurally similar compounds. It is almost inconceivable that in the case of a binary mixture composed of two substances so nearly alike as two isotopes, there should be a departure from normal behavior if only ideal distillation were involved. The only way to explain such a departure is to assume that a slight difference in the chemical properties of the two isotopes, such as a difference in the degree of association in the liquid state, is responsible. Thus, in the case of boron fluoride, the following equilibrium may exist in solution,

where the equilibrium constant for the above reaction is slightly greater than one, the B^{10} being a better electron "acceptor" than B^{11} . Therefore the boron fluoride vapor in equilibrium with this liquid will be slightly enriched in the B^{11} isotope and the $B^{11}F_3$ is thus made to appear more volatile than the $B^{10}F_3$. This reaction is similar to reactions described by Urey³ which are used for the separation of isotopes by the chemical exchange method.

In like manner, when methyl ether-boron fluoride complex is fractionated, B^{10} concentrates in the bottom. In this case, the complex itself is partially dissociated in the vapor state but is almost completely associated in the liquid state⁴. This might explain why the reported fractionation factor², 1.016, is much greater than that for boron fluoride and methyl borate. The separation of B^{10} and B^{11} may again be explained by the assumption that B^{10} is a better electron "acceptor" than B^{11} , in which case its complex is more strongly associated.

Thus, in the reactions

the equilibrium constant for reaction (3) is slightly greater than for reaction (4). The equilibrium existing in solution is represented by the following equation, obtained by subtracting equation (4) from equation (3):

where the equilibrium constant is slightly greater than one.

Now, since it has been postulated that the separation is due to a chemical reaction, it may then be assumed that the solution is ideal and that the physical properties of the two isotopic compounds do not differ sufficiently to account for the observed separation. Therefore, the equilibrium constant of reaction (5) may be expressed as:

$$K = \frac{N_{C^{10}B^{11}}}{N_{C^{11}B^{10}}} \quad (6)$$

where, $N_{B^{11}}$ and $N_{B^{10}}$ are the mole fractions of $B^{11}F_3$ and $B^{10}F_3$, respectively, in the liquid phase,
and $N_{C^{11}}$ and $N_{C^{10}}$ are the mole fractions of $Me_2O \cdot B^{11}F_3$ and $Me_2O \cdot B^{10}F_3$, respectively, in the liquid phase.

Since the solution is assumed to be ideal, Raoult's law applies, and the mole ratio, $N_{B^{11}}/N_{B^{10}}$, may be replaced by the ratio of the partial

pressures, $P_{B^{11}F_3}/P_{B^{10}F_3}$, of $B^{11}F_3$ and $B^{10}F_3$ in equilibrium with the liquid. K then becomes,

$$K = \frac{N_{C^{10}P_{B^{11}}}}{N_{C^{11}P_{B^{10}}}} \quad (7)$$

It is apparent from (7) that K is also the equilibrium constant of reaction (1).

But K is not equal to α , the simple process factor observed in the fractionation of complex, because it does not take into account the presence of undissociated complex in the vapor state. However, it is possible to express K in terms of α and the degree of dissociation of complex in the vapor phase by means of an equation derived as follows.

By definition, α is equal to the atomic ratio in the vapor phase divided by the atomic ratio in the liquid phase, or, expressed in the form of an equation,

$$\alpha = \frac{\frac{B^{11} \text{ in gas}}{B^{10} \text{ in gas}}}{\frac{B^{11} \text{ in liquid}}{B^{10} \text{ in liquid}}} \quad (8)$$

Since liquid complex is only slightly dissociated, the atomic ratio in the liquid phase is essentially equal to the mole ratio of undissociated complex, or,

$$\frac{B^{11} \text{ in liquid}}{B^{10} \text{ in liquid}} = \frac{N_{C^{11}}}{N_{C^{10}}} \quad (9)$$

The atomic ratio in the gas phase is equal to the sum of the partial pressures of free $B^{11}F_3$ gas and undissociated $Me_2O \cdot B^{11}F_3$ vapor divided by the sum of the partial pressures of free $B^{10}F_3$ gas and undissociated $Me_2O \cdot B^{10}F_3$ vapor, or,

$$\frac{B^{11} \text{ in gas}}{B^{10} \text{ in gas}} = \frac{P_{B^{11}} + P_{C^{11}}}{P_{B^{10}} + P_{C^{10}}} \quad (10)$$

where $P_{C^{11}}$ and $P_{C^{10}}$ are the partial pressures of undissociated B^{11} and B^{10} complex in the vapor phase.

Substituting equations (9) and (10) into (8), the following expression for α is obtained,

$$\alpha = \frac{N_{C10}}{N_{C11}} \times \left(\frac{P_{B11} + P_{C11}}{P_{B10} + P_{C10}} \right) \quad (11)$$

By using calculated data on the degree of dissociation of complex in the vapor state, and by substituting this value into the above equation, K can be expressed as a function of α and the degree of vapor dissociation. This is done in the following section where it is found that,

$$K = 1 + \frac{\alpha - 1}{\text{Fraction Dissociated.}} \quad (12)$$

CALCULATION OF THE EQUILIBRIUM CONSTANT, K

It has been postulated that in the fractionation of methyl ether-boron fluoride complex the solution is ideal and the physical properties of the two isotopic compounds are the same. Expressed in the form of equations, these assumptions are:

$$P_{C10} = P_{N_{C10}} \quad (13)$$

$$P_{C11} = P_{N_{C11}} \quad (14)$$

$$P_{B10} = H_{N_{B10}} \quad (15)$$

$$P_{B11} = H_{N_{B11}} \quad (16)$$

where, P and H are the Raoult's and Henry's law constants, respectively.

When these values are substituted in equation (9), the expression for α becomes,

$$\alpha = \frac{N_{C10}}{N_{C11}} \times \left(\frac{\frac{H}{P} \frac{N_{B11} + N_{C11}}{N_{B10} + N_{C10}}}{\frac{H}{P} \frac{N_{B11} + N_{C11}}{N_{B10} + N_{C10}}} \right) \quad (17)$$

The ratio $\frac{H}{P}$ can be eliminated from the above equation by making use of the known degree of dissociation of complex in the vapor state as measured by Brown and Adams⁵. From calculations made with their data, it has been shown⁶ that the degree of dissociation of saturated complex vapor is substantially constant over a range of temperatures and approximately equal to 60%. Therefore, the following relation between the partial pressures of the constituents of saturated complex vapor is true..

$$P_{B10} + P_{B11} = \left(\frac{.6}{1 - .6} \right) \times (P_{C10} + P_{C11}) = 1.5 (P_{C10} + P_{C11}) \quad (18)$$

Substituting equations (13), (14), (15), and (16) into (18), this equation becomes,

$$\frac{H}{P} = 1.5 \frac{(N_{C^{10}} + N_{C^{11}})}{(N_{B^{10}} + N_{B^{11}})} \quad (19)$$

This value for H/P can be inserted into equation (15) and the expression for α then becomes,

$$\alpha = \left(\frac{N_{C^{10}}}{N_{C^{11}}} \right) \frac{(1.5 N_{B^{11}} \left(\frac{N_{C^{10}} + N_{C^{11}}}{N_{B^{10}} + N_{B^{11}}} \right) + N_{C^{11}})}{(1.5 N_{B^{10}} \left(\frac{N_{C^{10}} + N_{C^{11}}}{N_{B^{10}} + N_{B^{11}}} \right) + N_{C^{10}}} \quad (20)$$

It is shown in the Appendix, Part I, that the above equation, by algebraic manipulation, can be reduced to the following,

$$K = 1 + \frac{\alpha - 1}{0.6} \quad (21)$$

If, $\alpha = 1.016$, K then = 1.027, which is the sought for value of the equilibrium constant of reaction (1).

DISCUSSION

In general, a mechanism gives a more detailed view of a system than does the statement of the overall reaction. Its value lies in the fact that it makes it possible to predict how the system will react to changing conditions.

For example, the mechanism outlined above predicts:

1. That the fractionating efficiency is dependent upon the degree of vapor dissociation, and that any factor, such as the presence of an excess of methyl ether, which lowers the degree of dissociation, also lowers the fractionating efficiency. This fact is not evident from the overall statement, and would not be predicted if it were assumed that the isotopic fractionation were due to a difference in volatilities of the B^{11} and B^{10} complexes.

2. That the difference between the normal boiling points of pure B^{11} and B^{10} complex is only 0.25°C . The details of this calculation are given in the Appendix, Part II. This boiling point difference is approximately one-half

that required by the assumption that the fractionation factor represents the ratio of the vapor pressures of the two pure liquids.

3. That the isotopic separation factor between boron fluoride gas and liquid complex is 1.027. If the fractionation of complex were to be explained merely by a difference in volatility of the B^{11} and B^{10} complexes, then the separation factor in the reaction of boron fluoride gas with liquid complex would be 1.000, and there would be no enrichment.

These predictions suggest a few experiments which could be made to test the validity of the postulated mechanism. Two such experiments were made and are described in the next section.

EXPERIMENTAL PART

Comparison of the Boiling Points of B^{11} and B^{10} Complex

The boiling point of methyl ether-boron fluoride complex containing 95% B^{10} was compared with that of normal complex (18.8% B^{10}) at atmospheric pressure in an experiment described in the Appendix, Part III. The postulated mechanism predicts a difference of about $0.2^{\circ}C$. in the boiling points while the assumption that $\alpha = 1.016$ represents the vapor pressure ratio of pure B^{11} and B^{10} complex would require approximately $0.4^{\circ}C$. difference. Actually, within the limits of sensitivity of the apparatus, no difference was found in the boiling points. There is some uncertainty in estimating the sensitivity of the potentiometer used but it was believed to be capable of detecting at least a $0.2^{\circ}C$. difference. Therefore, the results of this experiment, while not definitely conclusive, favor the chemical exchange mechanism rather than the other.

Isotopic Exchange Between Boron Fluoride Gas and Methyl Ether-Boron Fluoride Liquid

In this experiment, described in detail in the Appendix, Part IV, boron fluoride gas was shaken up with methyl ether-boron fluoride complex of the same isotopic composition. After equilibrium was reached, the boron fluoride was removed and its isotopic ratio was compared on the mass spectrometer with the isotopic ratio of the liquid. It was found that,

$$K = \frac{\frac{B^{11}(\text{gas})}{B^{10}(\text{gas})}}{\frac{B^{11}(\text{liquid})}{B^{10}(\text{liquid})}} = 1.025 \pm .002$$

Thus, the results of this experiment agree within experimental error with the value of $K = 1.027$ predicted by the mechanism assumed. If the separation of complex by fractionation occurred due to differences in volatilities, the K for this experiment would be 1.000.

CONCLUSIONS

1. A mechanism has been proposed to explain the isotopic fractionation occurring in the distillation of the methyl ether-boron fluoride complex.

2. This mechanism was used to calculate the equilibrium constant K for the reaction of boron fluoride gas with methyl ether-boron fluoride complex. The value of $K = 1.027$, calculated from $\alpha = 1.016$, was confirmed by an experiment in which K was found to be $1.025 \pm .002$.

3. This value of $K = 1.027$ is the proper factor to use in correcting B^{10} analyses of complex by the new rapid method.

A P P E N D I X

A P P E N D I X

PART I

CALCULATION OF THE EQUILIBRIUM CONSTANT

Equation (20) of the text,

$$\alpha = \left(\frac{N_{C10}}{N_{C11}} \right) \frac{(1.5 N_{B11} \frac{N_{C10} + N_{C11}}{N_{B10} + N_{B11}} + N_{C11})}{(1.5 N_{B10} \frac{N_{C10} + N_{C11}}{N_{B10} + N_{B11}} + N_{C10})}$$

simplifies to,

$$\alpha = \left(\frac{N_{C10}}{N_{C11}} \right) \left(\frac{2.5 N_{B11} N_{C11} + 1.5 N_{B11} N_{C10} + N_{B10} N_{C11}}{2.5 N_{B10} N_{C10} + 1.5 N_{B10} N_{C11} + N_{B11} N_{C10}} \right) \quad (1a)$$

Using the expression for K, equation (6),

$$\alpha = \frac{2.5 K + 1.5 K \frac{N_{C10}}{N_{C11}} + \frac{N_{C10}}{N_{C11}}}{2.5 \frac{N_{C10}}{N_{C11}} + K + 1.5} \quad (2a)$$

It appears from the above equation that α varies with the mole ratio of the isotopes. However, for values of K close to one (1 to 1.05) α is independent of the mole ratio. This can be shown as follows.

For a given isotope ratio the relation between α and K can be expressed by expanding equation (2a) in a power series,

$$\alpha = F(K) = F(1) + F^I(K-1) + \frac{F^{II}(1)}{2!} (K-1)^2 + \frac{F^{III}(1)}{3!} (K-1)^3 + \frac{F^{IV}(1)}{4!} (K-1)^4 + \dots (3a)$$

where, $F(K)$ is a power function of K

and F^I , F^{II} , F^{III} , etc. are the first, second, third, etc. derivations of the function.

The coefficients of equation (3a) are calculated as follows:
From equation (2a),

$$F(K) = \frac{2.5 K + 1.5 K \frac{N_{C10}}{N_{C11}} + \frac{N_{C10}}{N_{C11}}}{2.5 \frac{N_{C10}}{N_{C11}} + K + 1.5} \quad (4a)$$

Replacing K in the above equation by 1 the value of the first coefficient is obtained.

$$F(1) = 1 \quad (5a)$$

Differentiating (4a) with respect to K, $\frac{N_{C10}}{N_{C11}}$ being constant, the following value of the first derivative is obtained,

$$F'(K) = \frac{3.75 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2}{\left(2.5 \frac{N_{C10}}{N_{C11}} + K + 1.5 \right)^2} \quad (6a)$$

Substituting K = 1 in the above equation the value of the second coefficient is obtained,

$$F'(1) = \frac{3.75 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2}{6.25 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2} = \frac{1.5}{2.5} \quad (7a)$$

Differentiating (6a) with respect to K the following value for the second derivative is obtained,

$$F''(K) = - \frac{2 \times 3.75 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2}{\left(2.5 \frac{N_{C10}}{N_{C11}} + K + 1.5 \right)^3} \quad (8a)$$

Substituting K = 1 in the above equation the value of F''(1) is obtained.

$$F''(1) = - \frac{2 \times 1.5}{2.5^2 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)} \quad (9a)$$

Similarly, the value of $F'''(1)$ may be shown to be:

$$F'''(1) = \frac{3 \times 2 \times 1.5}{2.5^3 \left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2} \quad (10a)$$

Substituting the values of $F(1)$, $F'(1)$, $F''(1)$, $F'''(1)$, obtained in equations (5a), (7a), (9a), (10a), into equation (3a), the following relation between α and K is obtained.

$$\alpha = 1 + \frac{1.5}{2.5} (K - 1) - \frac{1.5}{2.5^2} \frac{(K - 1)^2}{\left(\frac{N_{C10}}{N_{C11}} + 1 \right)} + \frac{1.5}{2.5^3} \frac{(K - 1)^3}{\left(\frac{N_{C10}}{N_{C11}} + 1 \right)^2} - \dots \quad (11a)$$

When K is smaller than 1.05 as it is in the present case, all second degree and higher order terms become negligible and equation (11a) can be rewritten in a form independent of $\frac{N_{C10}}{N_{C11}}$,

$$\alpha = 1 + \frac{1.5}{2.5} (K - 1) = 1 + .6 (K - 1) \quad (12a)$$

$$\text{or } K = 1 + \frac{\alpha - 1}{.6} \quad (13a)$$

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PART II

CALCULATION OF THE DIFFERENCE IN VAPOR PRESSURES AND BOILING POINTS BETWEEN B¹¹ AND B¹⁰ COMPLEX

From a consideration of the assumptions made in postulating the mechanism it appears that there should be only a slight difference in boiling points between B¹¹ and B¹⁰ complex.

In the gas phase the following two reactions occur,

$$(1 - \alpha_{10}) \quad (\alpha_{10}) \quad (\alpha_{10})$$

$$(1 - \alpha_{11}) \quad (\alpha_{11}) \quad (\alpha_{11})$$

The sum of these two are expressed by the following overall reaction,

$$\text{where } K = \frac{K^{11}}{K^{10}} = 1.027$$

In systems containing pure B¹⁰ complex and pure B¹¹ complex,

$$K^{10} = \frac{\alpha_{10}^2 P_{10}}{1 - \alpha_{10}^2} \quad K^{11} = \frac{\alpha_{11}^2 P_{11}}{1 - \alpha_{11}^2}$$

where, P_{10} and P_{11} are the total pressures,

α_{10} and α_{11} are the degrees of dissociation* of the light and heavy forms in the gas phase at the pressure P_{10} and P_{11} .

From these relations it follows,

$$K = \frac{K^{11}}{K^{10}} = \frac{\alpha_{11}^2 (1 - \alpha_{10}^2) P_{11}}{\alpha_{10}^2 (1 - \alpha_{11}^2) P_{10}} = 1.027$$

(1b) 15

*In this part of the report the symbol α is used to denote the degree of dissociation, whereas in all other parts of the report α denotes the single plate fractionation factor. However, the α used in this part always has a subscript 10 or 11, which should avoid confusion.

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which reduces to,

$$\left(\frac{\alpha_{11}}{1 - \alpha_{11}} \right)^2 = 1.027 \left(\frac{\alpha_{10}}{1 - \alpha_{10}} \right)^2$$

or

$$\frac{\alpha_{11}}{1 - \alpha_{11}} = \sqrt{1.027} \left(\frac{\alpha_{10}}{1 - \alpha_{10}} \right) = 1.0134 \left(\frac{\alpha_{10}}{1 - \alpha_{10}} \right) \quad (7b)$$

If $\alpha_{10} = .630$, which is the approximate degree of dissociation of the methyl ether-boron fluoride complex at its normal boiling point⁶, 127°C., then,

$$\frac{\alpha_{11}}{1 - \alpha_{11}} = 1.0134 \times \frac{.63}{.37} = 1.7255$$

and $\alpha_{11} = .633$

which gives a difference of .003 in the degrees of dissociation of the two forms.

Dividing equation (4b) by (5b), an equation expressing the relative vapor pressures of both forms of complex as a function of the degree of dissociation in the vapor phase is obtained,

$$\frac{P_{11}}{P_{10}} = \frac{(1 + \alpha_{11})(1 - \alpha_{10})}{(1 + \alpha_{10})(1 - \alpha_{11})} \quad (8b)$$

At 127°C., when $\alpha_{10} = .630$ and $\alpha_{11} = .633$, equation (8b) becomes,

$$\frac{P_{11}}{P_{10}} = \frac{1.633 \times .370}{1.630 \times .367} = 1.010 \quad (9b)$$

But, from the equation for the vapor pressure of normal complex (18.8% B¹⁰) obtained by the SAM Laboratories²,

$$\log P = - \frac{2667}{T} + 6.64$$

the following equation can be derived,

$$\log (.188 P_{10} + .812 P_{11}) = - \frac{2667}{T} + 6.64 \quad (10b)$$

Replacing P_{11} by its value in terms of P_{10} given in equation (9b), and rearranging, the following expression for P_{10} is obtained,

$$\log P_{10} = - \frac{2667}{T} + 6.64 - \log 1.008 \quad (11b)$$

Replacing P_{10} in equation (11b) by its value in terms of P_{11} given in equation (9b), the following expression for P_{11} is obtained,

$$\log P_{11} = -\frac{2667}{T} + 6.64 - \log 1.008 + \log 1.010 \quad (12b)$$

At the boiling points T_{10} and T_{11} , $P_{10} = P_{11}$. Therefore, equating (11b) and (12b),

$$-\frac{2667}{T_{10}} + 6.64 - \log 1.008 = -\frac{2667}{T_{11}} + 6.64 - \log 1.008 + \log 1.010$$

or, simplifying,

$$T_{10} - T_{11} = \frac{T_{11} T_{10} \times .004321}{2667} \quad (13b)$$

But $T_{11} T_{10} = (273 + 127)^2 = 160,000$.

Therefore, equation (13b) becomes,

$$T_{10} - T_{11} = \frac{160000 \times .004321}{2667} = 0.26^\circ\text{C}.$$

Thus, at the normal boiling point it is predicted that there could be a difference of 0.26°C . between the boiling points of pure B^{11} and pure B^{10} complex.

Five Junction
Iron-Constantan
Thermocouple

Thermocouple
Well

Condenser

To Atmosphere
Via
Drying Trap

Copper Leads
To
Potentiometer

Receiver

Still Pot

Figure 1

APPARATUS FOR COMPARISON OF BOILING POINTS

A P P E N D I X

PART III

MEASUREMENT OF THE BOILING POINT DIFFERENCE BETWEEN B¹¹ AND B¹⁰ METHYL ETHER-BORON FLUORIDE COMPLEX

APPARATUS

A diagram of the apparatus used is shown in Figure 1. It consists essentially of:

Two simple stills, each made up of the following parts:

A still pot made from a 300-cc. round bottom flask.

An unpacked column, 16" long, made from 10 mm. pyrex tubing, connecting the still pot to the distilling head.

Distilling head, constructed from 20 mm. and 10 mm. tubing, containing a thermocouple well and a vapor delivery arm.

Water cooled condenser.

Receiver and vent. The vent is open to the atmosphere through a drying trap.

A five junction iron-constantan thermocouple calculated to give an EMF of 0.264 millivolts per degree centigrade.

A Leeds and Northrup Potentiometer Indicator sensitive to approximately 0.04 millivolts.

PROCEDURE

Approximately 200 ml. of redistilled methyl ether-boron fluoride complex containing 95% B¹⁰ was placed in one of the stills and the same amount of methyl ether-boron fluoride complex containing 18.8% B¹⁰ (normal complex) was placed in the other.

Heat was applied and both samples were distilled vigorously. Their boiling temperatures and temperature differences were measured at intervals by the five-junction iron-constantan thermocouple until most of the material in both flasks had distilled over. The two ends of the five-junction thermocouple were interchanged from time to time to eliminate any possible effects due to slight differences in construction.

RESULTS

After 20 cc. of each had distilled

Temp. of 95% material = $34.0 \text{ mv} \equiv 128^{\circ}\text{C}$.

Temp. difference between 95% and 18% = $0.00 \text{ mv} \equiv 0.0^{\circ}\text{C}$.

After 150 cc. of each had distilled

Temp. of 95% material = $34.0 \text{ mv} \equiv 128^{\circ}\text{C}$.

Temp. difference between 95% and 18% = $0.00 \text{ mv} \equiv 0.0^{\circ}\text{C}$.

DISCUSSION AND CONCLUSIONS

The potentiometer used was probably sensitive to 0.04 millivolts or in this case to a difference of 0.2°C . Therefore, it can be concluded from the results of the experiment that the boiling points at atmospheric pressure of the two isotopic liquids differ by 0.2°C . or less.

Figure 2

APPARATUS FOR PREPARATION OF ENRICHED BF_3

RECEIVED

A P P E N D I X

PART IV

MEASUREMENT OF THE ISOTOPE EXCHANGE CONSTANT BETWEEN
BORON FLUORIDE AND METHYL ETHER-BORON FLUORIDE COMPLEX

Boron fluoride was shaken with methyl ether-boron fluoride complex of the same isotopic composition. The resulting gas was then withdrawn and its isotopic ratio was compared on the mass spectrometer with the original gas and thus K was determined.

At the time this experiment was made, the mass spectrometer was being operated in a range suitable for analyzing samples with a high B^{10} content. Therefore, in order to avoid interfering with routine operation, it was necessary to carry out the exchange experiment with material rich in B^{10} instead of with normal material. . .

PREPARATION OF BORON FLUORIDE AND METHYL ETHER-
BORON FLUORIDE COMPLEX OF THE SAME ISOTOPIC COMPOSITION

Apparatus

The apparatus used (Figure 2) consisted of the following parts:

A manifold to which was connected a source of vacuum, a mercury manometer, a glass bulb C, the containers A and B through ground glass joints, and a copper-glass seal leading to a copper line and cylinder connection.

A glass bulb C made from 20 mm. tubing, of about 75 ml. capacity and sealed to the manifold via a stopcock.

A glass bulb B of about 50 ml. capacity made from 20 mm. tubing in two sections joined by a ground joint and sealed to the manifold through a stopcock. The lower part of this bulb is used for collecting the prepared complex.

A liter bottle A joined by a ground glass joint to a stopcock which was connected to the manifold by means of another ground joint. The bottle A is used for shaking up boron fluoride gas with liquid complex rich in B^{10} in order to prepare a large amount of enriched gas.

A bottle D which consisted of a 200 ml. round bottom flask fitted with a stopcock and a male ground glass joint. **This bottle is used for storing a portion of the enriched boron fluoride gas after it is prepared.**

Procedure

One hundred fifty ml. of methyl ether-boron fluoride complex of about 95% B^{10} content is placed in bottle A, which is then attached to the manifold at E and evacuated. Normal boron fluoride is then admitted from a tank attached to the cylinder connection until the pressure rises to about an atmosphere and a half. It is necessary to wire down the ground glass joints in order to keep them from being blown off. The stopcocks on both sides of joint E are closed, bottle A disconnected at E and shaken for fifteen minutes. At the end of this period bottle A is re-attached at E, liquid nitrogen placed around bulb C, and the enriched boron fluoride allowed to pass from A to C. Bottle A is then removed by disconnecting at E.

The boron fluoride is then distilled at a low temperature from C, which is kept at dry ice temperature, to B, cooled in liquid nitrogen, in order to remove any liquid complex which may have been carried over from A.

Bulb D is then attached to the apparatus at E and evacuated. A portion of the boron fluoride in B is allowed to expand into D. D is then removed and stored for future use.

An excess of methyl ether is then added from a cylinder to the boron fluoride stored in B. The material in B is kept at dry ice temperature and pumped on until all the excess methyl ether is removed. This is tested for by allowing bulb B to warm to room temperature and noticing the vapor pressure on the manometer. It will not be more than a few millimeters if all the methyl ether has been removed.

After all the methyl ether is pumped off, the bottom half of bulb B is removed, capped, and set aside for future use.

Results

When this procedure was followed, approximately 200 ml. of boron fluoride at 300 mm. pressure containing approximately 91.5% B^{10} , were obtained in bottle D, and about 5 cc. of methyl ether-boron fluoride complex of the same isotopic composition were obtained in bulb B.

Exchange Reaction Between the Gas and Liquid

This part of the experiment was carried out by C. M. Judson in the apparatus used in the new rapid method for B^{10} analysis¹.

A portion of the gas in bottle D was shaken with a portion of the complex from bulb B. After equilibrium had been reached a sample of the gas was drawn off for analysis on the mass spectrometer.

Mass Spectrometer Analyses

This part of the experiment was carried out by A. N. Webb.

The gas withdrawn from bulb B was compared on the mass spectrometer with the gas from bottle D. Thus, the gas in equilibrium with liquid complex was compared with the gas originally used in preparing the liquid complex. The relative quantities used were such that there was negligible change in composition of the liquid complex during the experiment. Therefore the samples analyzed represented the gas and liquid, respectively.

The results were:

$$\frac{\frac{B^{11} \text{ gas}}{B^{10} \text{ gas}}}{\frac{B^{11} \text{ liquid}}{B^{10} \text{ liquid}}} = 1.025 \pm .002$$

CONCLUSION

The value of K obtained on the mass spectrometer is sufficiently accurate to prove that the proposed mechanism, which predicts $K = 1.027$, is a correct interpretation of the isotopic fractionation.

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