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Thermal Diffusion with Boron Trifluoride*

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With BF_3 gas at atmospheric pressure in 7 meters of hot wire Clusius and Dickel columns, with $\Delta T = 400°C$, the equilibrium separation factor for $B^{10}F_3/B^{11}F_3$ was 1.32 ± 0.12, reached in slightly over three days. Our best separation factor per meter of column indicates a thermal diffusion constant $\alpha \cong +5.0 \times 10^{-4}$ and $R_T \cong 0.06$. Experience in purifying commercial BF_3 gas and with mass spectrometer analyses is discussed.

INTRODUCTION

BORON of mass 10 is of considerable interest in nuclear research because of its large cross section for the $B^{10}(n, \alpha)Li^7$ reaction. To increase the concentration of this isotope in some boron compound, it seemed possible that the thermal diffusion method, which has been so successful in numerous isotope separation experiments,[1] would serve. The only available gaseous compound stable over a sufficiently large temperature range is boron trifluoride. Unfortunately, since the coefficient of viscosity η of BF_3 has not been determined, the thermal diffusion constant could not be predicted, and hence the design of an efficient multi-stage Clusius and Dickel apparatus could not be calculated in advance.

Assuming for purposes of rough calculation, however, that η for BF_3 is about the same as for SO_2, a molecule of about the same molecular weight and size, one can estimate that for maximum separation factor (ratio of the remixing by diffusion to that by convection equal to 2) a Clusius and Dickel hot wire column with the mean temperature 600°K and the gas at atmospheric pressure should have a gap space between hot and cold surfaces of about 3.54 mm. Such a value of η (162 micropoises at 100°C) would mean that R_T, the ratio of α to the hard sphere value for these molecular masses, is close to zero. Experience has shown, however, that one can compensate for this small value of R_T by using a greater length of column in a multi-stage apparatus. Since for most efficient operation of thermal separation columns, the distance $2w$ between hot and cold walls should be somewhat greater than that calculated for maximum separation factor, we have used glass columns of 8 mm I.D. with 20-mil wires along their axes. This makes $2w = 3.75$ mm, a reasonable compromise value even in retrospect. The construction features of our glass columns were similar to those described in other recent research papers from this laboratory.[2–4]

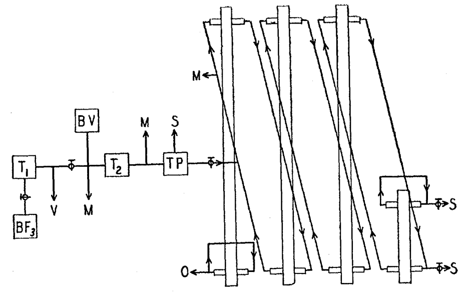

FIG. 1. Schematic diagram of thermal diffusion apparatus for boron trifluoride. Φ, steel valve; T_1, CO_2 trap, T_2, liquid-air trap (gas storage); *BV*, ballast volume; *TP*, Toepler pump; *M*, manometer; *O*, outlet to valve-off system; *S*, outlet to sampling system; *V*, vacuum pump.

SEPARATION APPARATUS AND PROCEDURE

Figure 1 is a schematic diagram of the thermal diffusion apparatus. The three long columns were each 3 meters in length, while the final shorter column was just 1 meter long. The top of each column was connected to the bottom of the succeeding column by a pair of convective coupling pipes, and convective circulation was maintained at the two ends of the apparatus. The first 3-

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[1] For a review and bibliography of the subject, cf., W. H. Furry and R. C. Jones, Rev. Mod. Phys. 18, 151 (1946).

[2] E. F. Shrader, Phys. Rev. 69, 439 (1946).

[3] S. B. Welles, Phys. Rev. 69, 586 (1946).

[4] R. Simon, Phys. Rev. 69, 596 (1946).

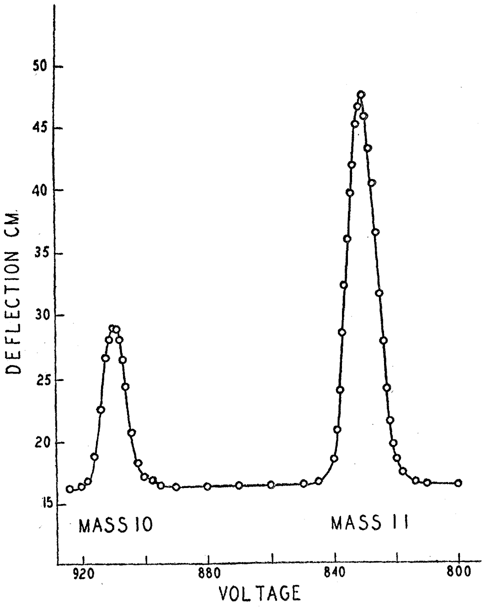

FIG. 2. B^+ mass peaks for BF_3 gas at "light" end of 7 meters of thermal diffusion column after 6 days of operation. B^{11}/B^{10} abundance ratio 2.92 to 1 as compared with 3.88 to 1 for the input "purified" gas.

meter column operated as a scrubber, the identical dimensions of the scrubber and the first separating column being in conformity with the dictates of the theory.[1] Both platinum and steel wires were used for the hot surfaces. Because of the concentration of a heavy, rather corrosive impurity, which was probably SiF_4, at the "heavy" end of the apparatus, we found it desirable to use platinum wire in the scrubber. At the "light" end of the apparatus, though, where this corrosive impurity was not present, we have found that the hot steel is not attacked at 450°C in an atmosphere of BF_3 gas. All valves were of steel.

It is of course essential for isotope separation by thermal diffusion that the working gas be pure. Our mass spectrometer analysis showed that commercial BF_3 gas contains very appreciable amounts of SiF_4, CO_2, N_2, and SO_2, the SiF_4 being the major impurity as judged by a large mass 85 peak assignable to SiF_3^+. To rid the gas as far as possible of these impurities we carried out several vacuum distillations at dry ice and liquid-air temperatures between traps T_1 and T_2 (Fig. 1). The purified gas was then stored at liquid-air temperature in T_2 from which portions were removed periodically to fill a modified Toepler pump. By means of compressed air through a slow leak, the gas was then forced continuously at the average rate of 55 cm^3/hr. from the Toepler pump into one of the convective coupling pipes connecting the scrubber and the first separating column. Samples could be taken in break-seal tubes of our input gas, as well as of the gas continuously exhausted at the bottom of the scrubber, and the gas both at the bottom and top of the final 1-meter column. The wire temperatures were set at 450°C by cathetometer measurement of the elongations produced by the heating current. The power consumption in the hot wires was 8 watts per meter.

This apparatus, with various minor modifications, was operated for different periods of time, the longest of which was 15 days. Even though we had taken great care to purify the BF_3 gas, we found upon shut-down after the 15 days of operation that the wire of the scrubber was coated with a corrosive deposit of solid material, and that a similar deposit, decreasing in amount with distance from the top of the scrubber, existed on the wires of the two 3-meter columns. The wire of the final 1-meter column at the "light" end, however, had no trace of a deposit on it. To explain this deposit we note that it must have come from an impurity heavier than BF_3 since it was being sent to the "heavy" end of the apparatus by the thermal syphoning action. Comparison of our mass spectrometer analyses of gas samples taken from the bottom of the scrubber and from the "light" end of the separating columns indicated, by the presence of a mass 85 peak in the former and its absence in the latter, that SiF_4 was probably the responsible impurity.

It would undoubtedly be possible to purify the BF_3 gas more completely, and then any slight residue of SiF_4 should be practically completely bled-off at the bottom of the scrubber. Our purification process does seem to have effectively removed all the nitrogen. According to our analyses of the gas at the bottom and top of the 1-meter column, quite pure BF_3 was circulating in this part of our system. The best separation factor was produced in this last meter of separating column, and we therefore draw our conclusions almost entirely from its performance.

MASS SPECTROMETER ANALYSES

All of the gas analyses were carried out with a small 60° mass spectrometer modeled after one described by Nier.[5] No trouble was experienced from any corrosive action of BF_3 or SiF_4. In agreement with the findings of Inghram,[6] we observed that BF_2^+ and SiF_3^+ are by far the most abundant positive ions of all those formed by the electron impacts in the ion source of the spectrometer. Because the peaks at mass 10 and mass 11 were better resolved and were uninfluenced by overlapping of other mass peaks, however, we used them exclusively in our determination of the relative abundance of the two boron isotopes in all samples. Figure 2 is representative of the performance of our spectrometer. This particular analysis was of a gas sample withdrawn from the top of the 1-meter column after 6 days of operation, the ratio of the heights of the B^{11} and B^{10} peaks being 2.92 to 1, after the correction for the difference in accelerating voltage is applied, as against 3.88 to 1 for the input "purified" gas.

Since we varied the accelerating voltage in the ion source in order to bring the desired positive-ion masses into the collector of the spectrometer, it is incorrect to compute the abundance ratio directly from the ratio of the observed peak heights. The magnitude of the correction to be applied to give true abundance ratios was determined experimentally by holding the accelerating voltage constant and varying the field of the main deflecting magnet. For small ion masses such as 10 and 11 this voltage correction is very appreciable. Our measured abundance ratio of 3.88/1 for B^{11}/B^{10} in the input BF_3 gas is surprisingly low, since the accepted normal abundance ratio for B^{11}/B^{10} is 4.31/1,[6] and we did get that higher ratio for one lot of specially purified gas which was made available to us. Nevertheless, by taking the ratio of the abundance ratios at the two ends of our columns determined with our mass spectrometer under identical conditions, the correct separation factors for these experiments should result.

EXPERIMENTAL RESULTS

The separation factors for $B^{10}F_3/B^{11}F_3$ determined in this manner during the 15-day run with this apparatus are given in Table I. It is evident that the equilibrium separation factor for the 7 meters of column was about 1.32 ± 0.12, the equilibrium being attained in slightly over three days. That the 7 meters of column should have produced a higher factor than this is shown, for one thing, by the fact that from the samples drawn off at the 6-meters point we determined the factor there to be about 1.21. Now the equilibrium separation factor should vary exponentially with the length of separating column. Taking the ratio of the logs of these factors for $L=7$ meters and 6 meters, we get 0.120/0.080, or 4/3 rather than 7/6. Thus it would seem that the final 1-meter column at the "light" end was functioning satisfactorily, but that the operation of the first 3-meter separating column was being impeded by the presence of a considerable amount of the heavy impurity. We should therefore draw our conclusions from the performance of the "light" end of the apparatus only. Judging from these best results, we can state that with $\Delta T = 400°\text{C}$ between the hot wire and surrounding cold wall of a Clusius and Dickel column using BF_3 gas at atmospheric pressure, and with $2w = 3.75$ mm, the separation factor for $B^{10}F_3/B^{11}F_3$ per meter of column is close to 1.1. There was about $\frac{3}{4}$ g of gas in the end volume at the "light" end of the apparatus.

From our observed separation factors we are certain that the thermal diffusion constant α for BF_3 is small but positive. To estimate the value of α, we take 1.1 as the equilibrium separation factor q_e per meter of column, solve for the A constant ($q_e = e^{2AL}$), then assume the viscosity the same as for SO_2 (1.62×10^{-4} poise). This calculation indicates that $\alpha \cong 5.0 \times 10^{-4}$, and therefore R_T, the ratio of α for this molecule to that for a hard sphere molecule of the same mass, is about 0.06. The smallness of this value means that the

TABLE I. Separation factors for $B^{10}F_3/B^{11}F_3$ produced by 6- and 7-meters of hot wire thermal diffusion column for $\Delta T = 400°\text{C}$, $p = 1$ atmos., and $2w = 3.75$ mm.

t	$L=6$ meters	$L=7$ meters
3 days	—	1.295 ± 0.117
6	1.205 ± 0.128	1.330 ± 0.126
9½	—	1.303 ± 0.122
12	1.220 ± 0.091	1.290 ± 0.136
15	—	1.343 ± 0.128

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[5] A. O. Nier, Rev. Sci. Inst. 11, 212 (1940).

[6] M. G. Inghram, Phys. Rev. 70, 653 (1946).

repulsive force index is but little over the critical value of 5. Undoubtedly the BF_3 molecule becomes "harder" at higher temperatures, as has been noted[7] for NH_3, but one is limited in temperature by the possibilities of increased chemical reactivity and decomposition. We conclude that concentrated B^{10} material may surely be obtained by the thermal diffusion method, but with an over-all efficiency of the plant much too low to make the job attractive.

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[7] W. W. Watson and D. Woernley, Phys. Rev. **63**, 181 (1943).

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Dielectric and Piezoelectric Properties of Barium Titanate[*]

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The dielectric constant and loss of barium titanate and barium-strontium titanate have been measured at biasing field strengths from 0 to 5 megavolts per meter, at temperatures from −50°C to +135°C and at frequencies from 0.1 to 25 megacycles. The measurements *versus* temperature indicate the expected agreement with the Curie-Weiss law at temperatures above the Curie point. Measurements *versus* field strength indicate that the electric field intensity can be expressed as a simple function of the electric displacement, consisting of a linear and a cubic term. At temperatures below the Curie point the results are more complicated, presumably because there are spontaneously polarized domains which give rise to hysteresis and remanence. At field strengths low enough to avoid hysteresis and remanent polarization, no anomalies in the dielectric characteristics *versus* frequency have been observed. When polarized, however, by a momentary application of a strong d.c. field, a resonance spectrum appears in these ceramics. These resonances are attributed to a piezoelectric effect which exists only in the polarized samples. The piezoelectric voltage developed upon squeezing a specimen of polarized barium titanate has been measured directly with a vacuum tube electrometer. Both the longitudinal effect (electric field parallel to mechanical stress) and the transverse effect (field perpendicular to stress) have been observed.

INTRODUCTION

While surveying the properties of a number of titania ceramics, Wainer and Salomon of the Titanium Alloy Manufacturing Company noticed anomalous polarization effects in barium titanate and in solid solutions of barium-strontium titanate.[1] Further studies in the Laboratory for Insulation Research established that these materials constitute a new class of ferroelectric dielectrics.[2,3] $BaTiO_3$ was shown to have a Curie point at about 116°C, coinciding with a lattice transformation from cubic to a structure of lower symmetry, which Megaw and Rooksby[4] identified as tetragonal. The addition of strontium titanate shifted the Curie point and the lattice transformation to lower temperatures. This shifting of the Curie point was followed by Jackson[5] down to −190°C for a composition containing 80 percent strontium titanate. Two additional singularities resembling Curie points have

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[2] N.D.R.C. Rep. Div. 14, No. 300, Aug., 1944; N.D.R.C. Rep. Div. 14, No. 540, Oct., 1945.

[3] A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, Ind. Eng. Chem. **38**, 1097 (1946).

[4] H. D. Megaw, Nature, **155**, 484 (1945); **157**, 20 (1946); Proc. Phys. Soc. Lond. **58**, 133 (1946). H. P. Rooksby, Nature **155**, 484 (1945).

[5] W. Jackson, and W. Reddish, Nature **156**, 717 (1945).