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# THE CHEMICAL EFFECTS

## OF

## 1 Mev ELECTRONS ON BrF₃ AT 25° C

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## ABSTRACT

An investigation of the chemical effects of 1-Mev electrons on $BrF_3$ at 25° C has been carried out. Pressure measurements taken during the irradiation suggested the presence of $Br_2$ and $BrF_5$ as decomposition products and a fractional distillation of the irradiated liquid confirmed their presence. The extent of decomposition was determined both by fractional distillation and spectrophotometric methods. The radiation effect seemed to reach saturation when approximately 10 per cent of the $BrF_3$ was destroyed. The exposure necessary for the decomposition products to reach a concentraction of half the saturated value was calculated to be 2.7 microampere hours/cc $BrF_3$, while the "G" value was found to be 1.5. A qualitative comparison of irradiation dosages from the Statitron with that expected from spent fuels revealed that little decomposition of $BrF_3$ reagent is to be expected from 1-day cooled Hanford fuel (in pile for 100 days) while in the case of 1-day cooled MTR type fuel (in pile for 12 days) a saturated effect might be realized in 1-3 hours. Since at most only 10% of the $BrF_3$ is destroyed it is concluded that $BrF_3$, from a radiation resistance standpoint, is a suitable reagent for the processing of short cooled fuels.

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# I. INTRODUCTION

Since the first reactors went into operation, one of the major problems has been the separation and recovery of fissionable materials from partially spent fuel. One of the recent approaches to fuel recovery is the bromine trifluoride volatility process.[1]

Some understanding of the effect of radiation on the chemical reagents used in the process is mandatory since reactions may be either inhibited or vastly accelerated by radiation fields. To supplement the considerable effort which has been directed toward the $BrF_3$ fluoride volatility process, a study of the radiation chemistry of $BrF_3$ was undertaken.

To simulate the effect of the heavily ionizing radiation fields from high burn-up fuel, the NAA Statitron (Van de Graaf Generator) was utilized. This machine is capable of delivering up to 30 microamperes/$cm^2$ of 1-Mev electrons (corresponding to an electron beam of about 5,000 curies/$cm^2$). It will later be shown that this radiation intensity exceeds that produced by most short cooled fuels (1-day decay time) from present day reactors. Thus, information from this study can be applied in evaluating the use of $BrF_3$ on short cooled Hanford and MTR type fuel.

Since combination between BrF or $Br_2$ and $F_2$ to form $BrF_3$ is known to be rapid,[2,3] it was believed at first that radiation effects would be small and would be detectable during the irradiation only. For this reason, pressure measurements taken during the irradiation with 1-Mev electrons constituted the first experiments. Pressure rises were observed in all cases. Since the final pressure was greater than the original pressure, it was concluded that stable decomposition products, which do not react at room temperature to generate $BrF_3$, were produced. In particular, $Br_2$ and $BrF_5$ were likely products since recombination of these compounds to form $BrF_3$ at room temperature is negligible.[4] A fractional distillation of the irradiated liquid resulted in the isolation of two low boiling fractions. One was a dark red liquid boiling at 34° C, and the other a colorless liquid boiling at 42° C. These same fractions were observed when a dilute solution of $Br_2$ in $BrF_5$ was distilled. The analytical results on F/Br ratios also pointed to the fact that $Br_2$ and $BrF_5$ are the predominant products formed during the irradiation of $BrF_3$ by energetic electrons.

Quantitative determinations of the extent of $BrF_3$ decomposition, both by chemical analysis of the products and by a spectrophotometric determination of the $Br_2$ in the irradiated liquid indicated that the radiation effect with 1-Mev electrons reached saturation when approximately 10% of the $BrF_3$ had been destroyed. Thus, it appears that $BrF_3$, from a radiation resistance standpoint, is a suitable reagent for the processing of short cooled fuels.

## II. GENERAL EXPERIMENTAL

### A. Source of Radiation

One-Mev electrons were generated by the NAA Statitron (Van de Graaf Generator). Beam intensities ranged from 5 to 25 microamperes. The total dosage was recorded by an electronic integrating circuit while the voltage was measured by a generating voltmeter. The Statitron power calculated from the voltmeter and ammeter readings deviated only about 10% from the power obtained by a calorimeter determination. (For details of the power calibration, see Appendix A.)

### B. Irradiation Cells

Two different irradiation cells were used in the experiments discussed in this report. The first one was used mainly for the preliminary runs in which pressure determinations were the essential point of the experiment while the other cell was used in irradiations in which the decomposition products were identified and the extent of radiation damage determined.

The first cell shown in Fig. 1 consisted mainly of a hollow 2S aluminum cylinder which contained the 7 cc of liquid $BrF_3$. A 1- to 2-mil aluminum window sandwiched between two thin Teflon gaskets and placed over the hollow cell was thin enough to prevent excessive attenuation of the beam and yet was strong enough to prevent accidental contact between $BrF_3$ and the Statitron. (For further details concerning the aluminum windows, see Appendix B.) A thermocouple well also constructed of 2S aluminum penetrated the wall of the cell into the $BrF_3$. Mechanical stirring was effected by a magnetic stirrer and a nickel agitator. The heat exchanger consisted of an aluminum jacket welded to the floor of the reaction vessel. Gaseous nitrogen cooled by a bath of liquid nitrogen was selected as a coolant in place of water for safety reasons.

PUMP OUTLET

VALVE

Br F$_3$ INLET

BOOTH-CROMER
PRESSURE GAUGE

1/16-in TEFLON GASKETS

1 MIL ALUMINUM
WINDOW

BEAM

STATITRON FLANGE

COOLING SYSTEM

Ni STIRRER

THERMOCOUPLE WELL

MAGNETIC STIRRER
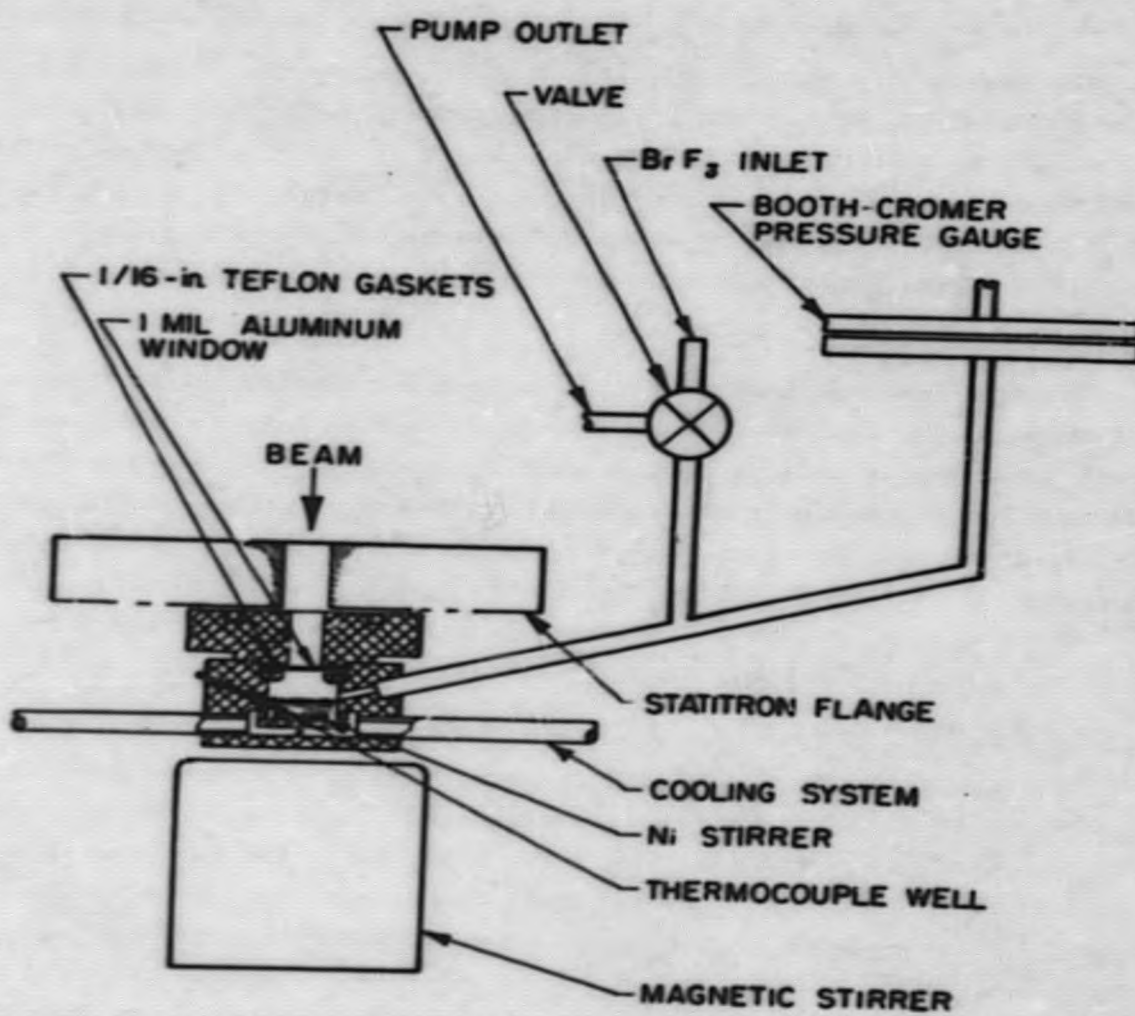
Fig. 1. Schematic Drawing of Irradiation Cell

A constant temperature (25° C) during the irradiation was accomplished with the use of 2 solenoid valves and a Bristol Electronic Free Vane Controller, Model #E-486, which was actuated by an iron-constantan thermocouple.

The pressure of the system was measured with a Booth Cromer gauge[5] which consists of an electronic pressure transmitter and self-balancing relay.

The second irradiation cell, shown in Fig. 2, was essentially a pair of thermostatted cells, one of which was exposed to the electron beam while the other served as a blank. Each of these cells contained 5 cc $BrF_3$. A chromel-alumel thermocouple inserted through the Teflon gasket directly into the $BrF_3$ (Fig. 3)* permitted more accurate temperature control. Fluorothene windows permitted a visual inspection of the cell contents before and after irradiations.

## C. Distillation Column

For experiments in which the decomposition products were separated by distillation, a Vigreaux distillation column, shown in Fig. 4, was used. This consisted of a Vycor column with several thermocouple wells. The lower Pyrex condenser jacket was electrically heated to the same temperature as that of the refluxing liquid to achieve an adiabatic state. The upper Pyrex jacket permitted the passage of cold air for refluxing and could be heated to distill the fraction into a Vycor collection tube. For reasons of safety, the Pyrex jackets were held in place with Teflon discs rather than cork or rubber.

## D. Spectrophotometer Cell

The visible absorption spectrum of the irradiated solution was obtained with a Beckman Model D.U. spectrophotometer. In order to accomplish this, it was necessary to have a cell which was resistant to the action of $BrF_3$. Such a cell, shown in Fig. 5, is a Teflon block containing four compartments. Two plates of 1/16-inch thick Fluorothene, clamped tightly against the Teflon by means of aluminum plates, served as the windows. The path length of the material in the cell was 1 centimeter. Teflon plugs prevented the escape of corrosive vapors. Thus, the $BrF_3$ came in contact with Teflon and Fluorothene only.† From a safety viewpoint $C_7F_{16}$, a colorless liquid, was used as a reference solution in place of water.

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*The chromel-alumel thermcouple showed no signs of corrosion after being immersed in the liquid $BrF_3$ for 2 weeks at room temperature.

†The optical densities of $Br_2$-$BrF_3$ solutions in this cell remained unchanged for more than 3 days.
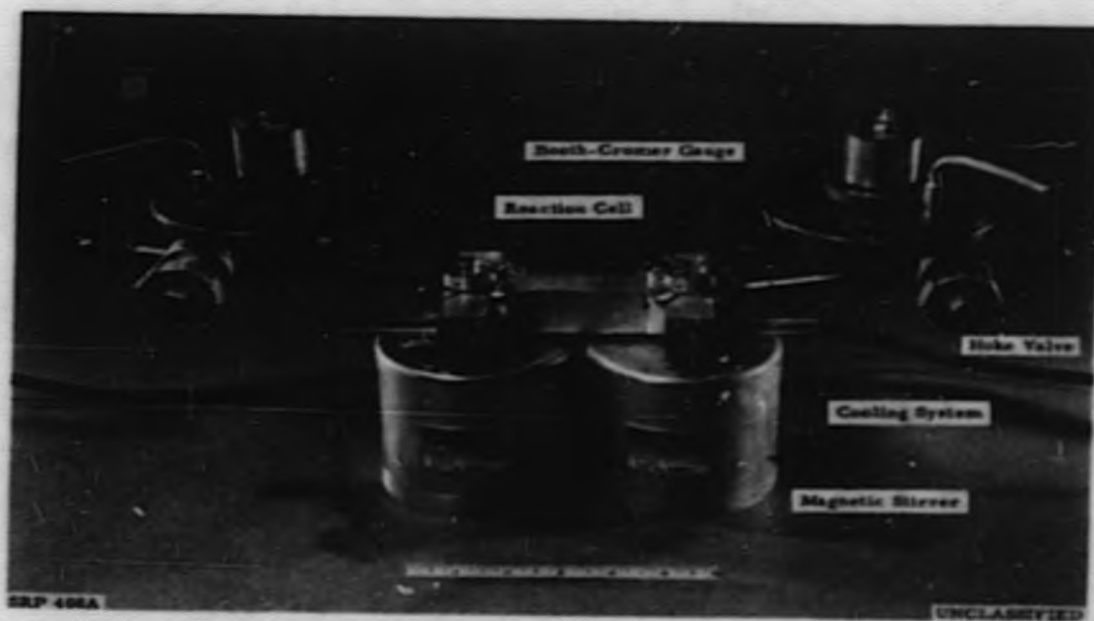
Fig. 2. Modified Apparatus for Statitron Irradiation of $BrF_3$



Fig. 3. View of Irradiation Cell Showing Fluorothene Window and Thermo-
couple

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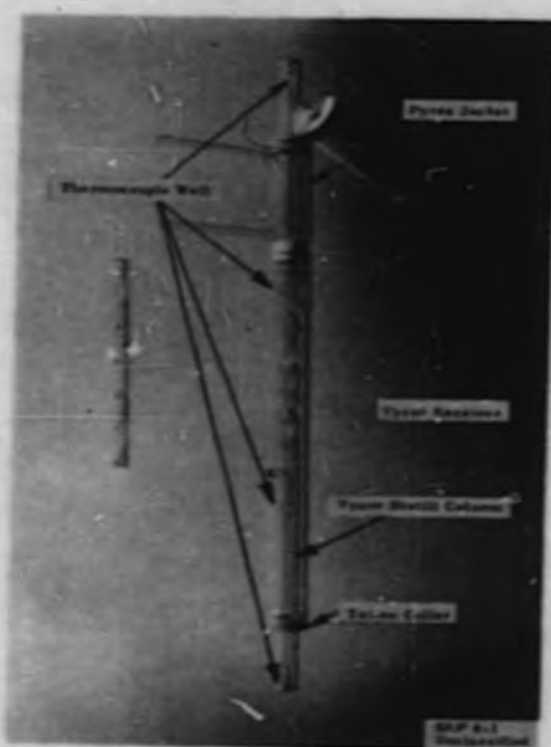
Fig. 4. Vycor Vigreaux Distillation Column

### E. Procedure

The cell was prefluorinated with $ClF_3$ at 100° C. The $BrF_3$ was introduced into the evacuated cell and the gases removed by intermittant pumping until the vapor pressure of the liquid was that of $BrF_3$ at 25° C (10 mm Hg) and until the pressure rise was less than 1 mm/hr. The cell was then attached to the Statitron and irradiated during which time pressure measurements were taken. For those experiments in which analytical data were obtained, some of the irradiated liquid was transferred by means of a Fluorothene pipette into the spectrophotometer cell for $Br_2$ analysis while the remaining liquid was transferred into the Vigreaux distillation column for fractional distillation. The fractions were treated with anhydrous sodium carbonate in a Fluorothene bag and analyzed for total bromine. (For details of this procedure, see Appendix C).
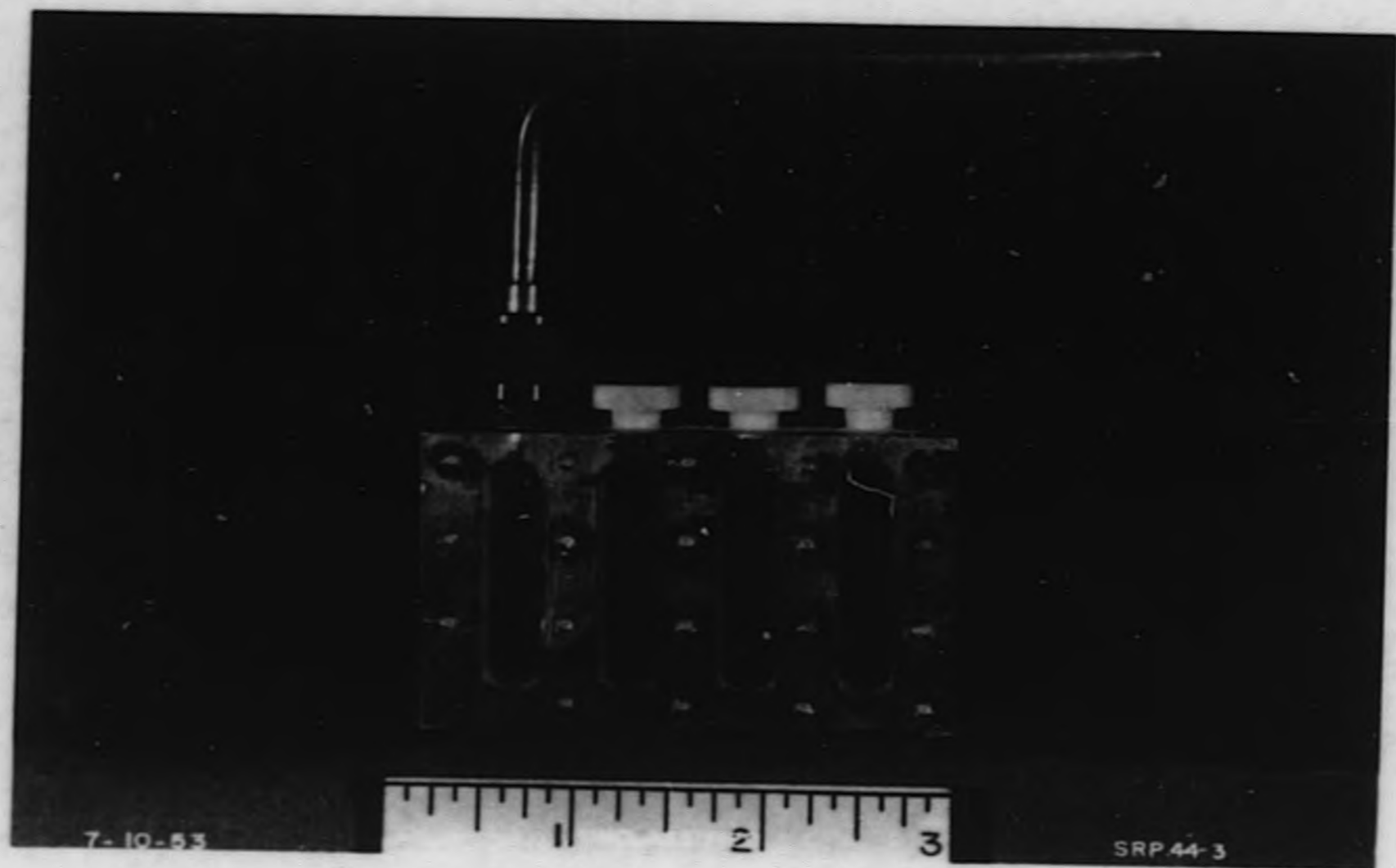
Fig. 5.  Spectrophotometer Cell

## III.  PRESSURE RISE EXPERIMENTS

### A.  Effect of Irradiation on Pressure

In all irradiations pressure increases were observed.  The effect of beam intensity on pressure rise is seen in Fig. 6.  The circles denote the pressure measured during the irradiation while the crosses indicate pressure measured in the absence of the electron beam.  As was expected, the rate of pressure rise increases with higher beam intensities.  The curves also show that the rate of pressure rise continues to decrease with time.  This suggested the possibility that a steady state was being approached.  In order to examine this possibility, $BrF_3$ was irradiated for 6-1/2 hours with a 15-microampere beam (100 microampere hours. )  The pressure curve shown in Fig. 7 suggests more strongly that a steady state was being approached.  Immediately after the removal of the beam, the pressure dropped from the maximum of 220 mm Hg to reach a constant value of 176 mm Hg.

### B.  Discussion of Results

The pressure data described above were useful in obtaining a clue as to the predominant over-all decomposition reaction.  At least four decomposition reactions come to mind:

$$2BrF_3 \longrightarrow Br_2 + 3F_2 \qquad \ldots \ (1)$$

$$BrF_3 \longrightarrow BrF + F_2 \qquad \ldots \ (2)$$

$$2BrF_3 \longrightarrow BrF + BrF_5 \qquad \ldots \ (3)$$

$$5BrF_3 \longrightarrow Br_2 + 3BrF_5 \qquad \ldots \ (4)$$
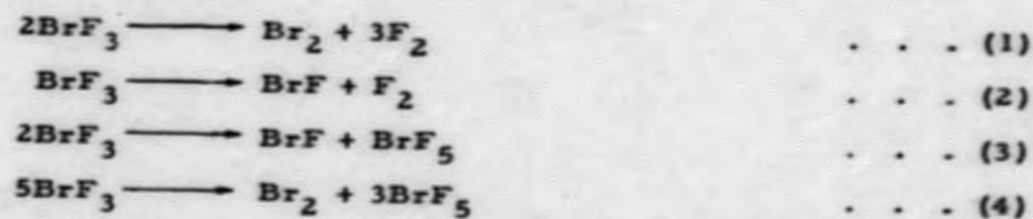
Since $Br_2$ and $F_2$ are known to recombine rapidly to regenerate the condensable $BrF_3$,[2,3] and since the pressure shown in Fig. 6 remains high (176 mm Hg) after the irradiation, Eq. 1 appears to be ruled out as the over-all reaction.  Although not much is known of the chemistry of BrF, one would expect the reaction between BrF and $F_2$ to be rapid.  Thus we shall not consider reactions (1) and (2).  Additional evidence to substantiate this decision was the result of the following experiment:  After the irradiation in which the pressure had risen to about 80 mm Hg, the cell was cooled from 20° to 0°C.  The pressure
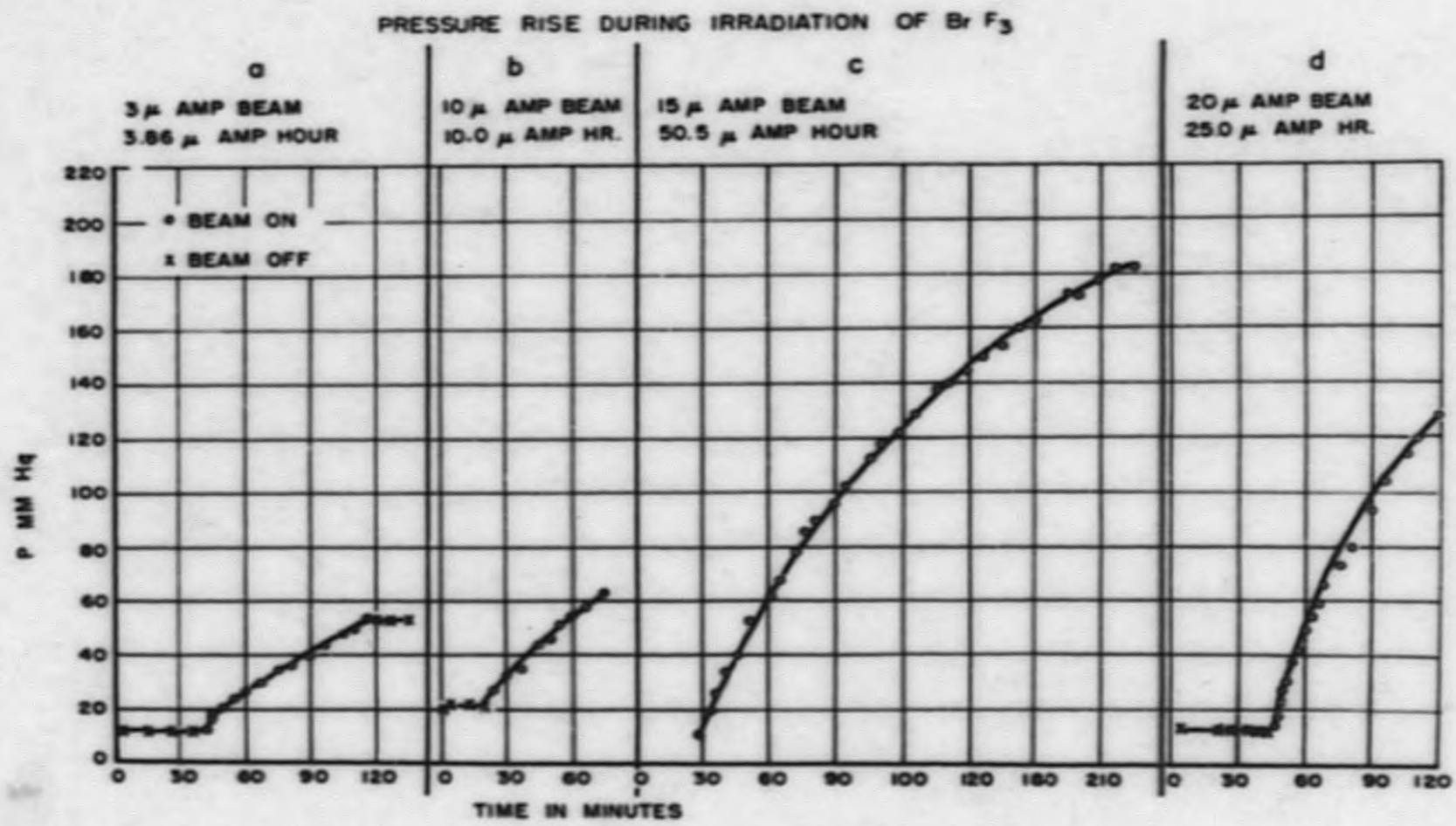
Fig. 6. Pressure Rise During Irradiation of BrF$_3$
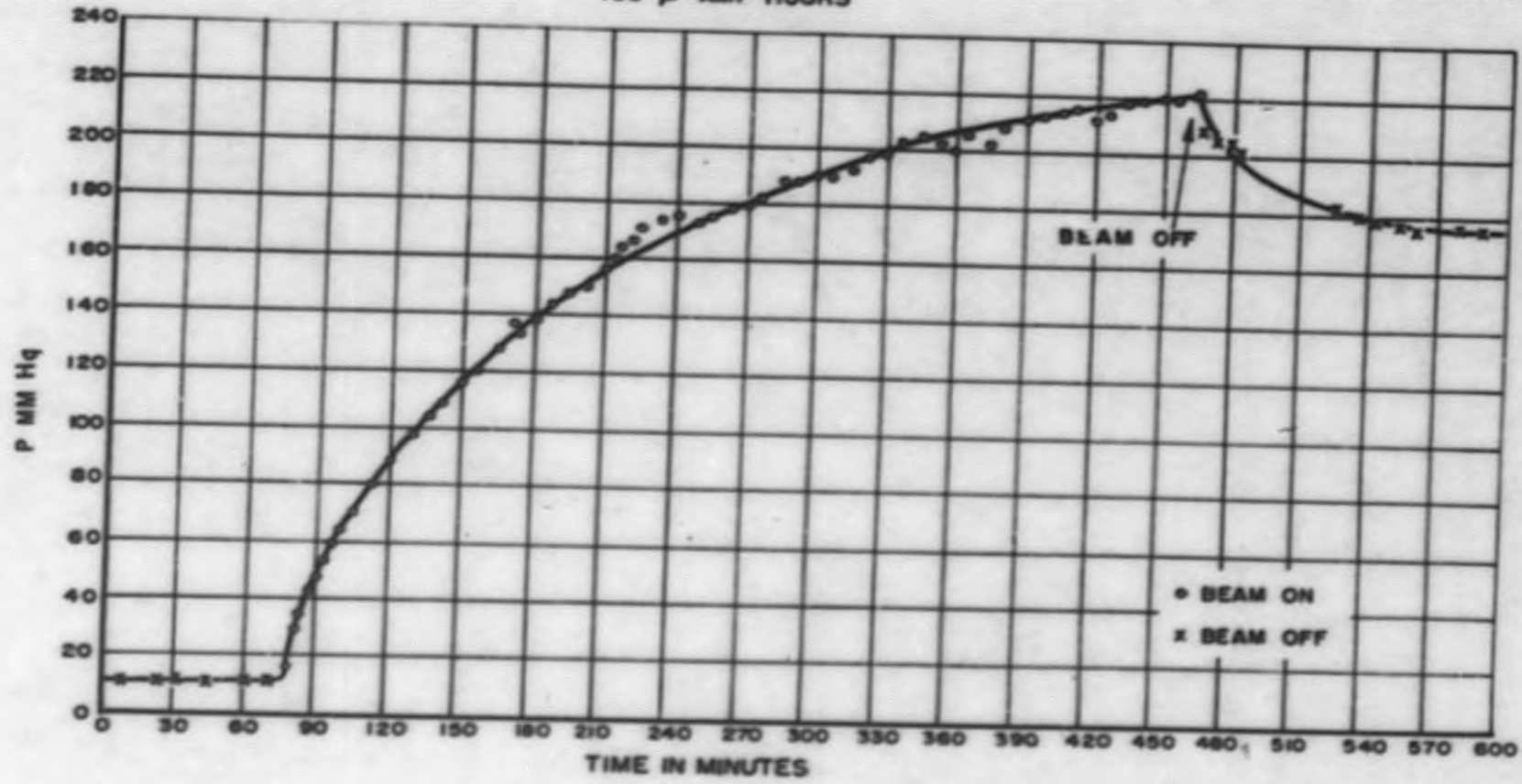
Fig. 7. Pressure Rise During Irradiation of $BrF_3$

dropped from 80 mm to approximately 30 mm Hg.* If the atmosphere of the cell had been mainly "non-condensable" gases, as would be the case for reactions (1), (2) and possibly (3), the decrease in pressure would have been far less. Thus, only reactions (3) and (4) remain as possibilities of the over-all decomposition reaction. Since BrF, if formed, is likely to disproportionate into $Br_2$ and a higher fluoride,[2] reaction (4) would appear to be the most likely one. Additional evidence for (4) is the fact that when the gases were pumped from the system, bromine was visible in the cold trap, although it is conceivable that BrF might have been decomposed enroute to the trap to form bromine. The presence of $Br_2$ and $BrF_5$ would be compatible with the fact that the rate of reaction between these compounds to form $BrF_3$ is negligible at room temperature.[4]

Unfortunately, the pressure data alone are not sufficient to permit even an estimate of the extent of destruction of $BrF_3$, for little is known of the vapor pressure of the $BrF_3$, $Br_2$, $BrF_5$ ternary system. Further, any corrosion of the cell by $BrF_3$ leading to the production of the "permanent gases" such as oxygen, results in a considerable error. For these reasons emphasis was then placed on more direct methods of both identification of the decomposition products and quantitative determinations of the extent of irradiation damage.

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*Since the decomposition products of $BrF_3$ seem to be volatile liquids, an explanation of the shape of the curves after the beam was shut off (Fig. 6) is suggested. The rapid pressure drop is due to a great extent to the following reasons: During the irradiation it is necessary to keep the bulk metal of the cell relatively cold in order to maintain the temperature of the $BrF_3$ at 25° C. As soon as the beam is turned off, the temperature of the liquid drops to that of the cell. It has already been shown that the vapor pressure of the irradiated liquid is very temperature dependent.

However, the final pressure (176 mm) was lower than that just before the beam was turned off (220 mm). This suggests that a thermal recombination of some of the decomposition products to regenerate $BrF_3$ is occurring. This might be a back reaction of the side reactions (1), (2),[3] or (3). Another explanation, however, is the following: essentially all of the power of the electron beam (15 watts in this case) is dissipated into a layer of $BrF_3$ less than 2 millimeters deep over an area a little over 1 $cm^2$. Despite the vigorous agitation of the liquid due to stirring, the top layer may be several degrees warmer than the bulk liquid in which the thermocouple well is immersed. Thus, when the beam is turned off, the pressure drops to that corresponding to the equilibrium temperature.

## IV. EXPERIMENTS INVOLVING THE IDENTIFICATION
## OF DECOMPOSITION PRODUCTS BY FRACTIONAL DISTILLATION

### A. Low Boiling Fractions Formed by Radiation

In the preceding section evidence based on pressure measurements was described pointing to the possibility that the decomposition products, formed during the irradiation of $BrF_3$ were mainly $Br_2$ and $BrF_5$. It was desirable to identify these products in a more direct manner. A visual inspection of the cell contents after two irradiations revealed extensive color changes. In the case of a 25-microampere hour (20-microampere beam) irradiation, the color of the liquid changed from the usual canary yellow to a deep transparent red. The color of the liquid after a 105-microampere hour (15-microampere beam) irradiation was also deep red. However, in this case the liquid appeared practically opaque. Thus it appeared that radiation damage was extensive enough to permit isolation of the products by a fractional distillation. If $Br_2$ and $BrF_5$ were the final products, the first fraction to distill over should be $BrF_5$, a colorless liquid boiling at 42° C,[6] followed by $Br_2$, a dark red liquid boiling at 59° C.[7] The final fraction should then be the yellow $BrF_3$ boiling at 126° C.[8] Actually the first fraction seen was a dark red liquid which wet the glass and condensed at 34° C. This was followed by a water-white liquid boiling at 42° C which also wet the glass. Finally, a yellow liquid which boiled at 127° C and which did not wet the glass was observed.

There was little doubt that the colorless liquid boiling at 42° C was $BrF_5$ and that the yellow liquid boiling at 127° C was $BrF_3$. However, the boiling point of the dark red liquid (34° C) was not the same as that of bromine (59° C) or any known bromine-fluorine compound. To test the possibility that the liquid was an azeotrope, boiling points of synthetic binary mixtures of the $Br_2$-$BrF_3$-$BrF_5$ system as well as each component were determined in the same manner as those of the irradiated liquid. The fractions observed are shown in Table I.

The crosses in the table denote that a fraction with the properties indicated in the heading was observed in the corresponding mixtures. Two fractions were observed with boiling points different from those of $Br_2$ (59° C), $BrF_5$ (42° C) and $BrF_3$ (126° C). One of these found when a mixture of $Br_2$ and $BrF_3$ was distilled, was a dark red liquid which did not wet the Vycor surface and boiled

## TABLE I

### BOILING POINTS OBSERVED IN THE DISTILLATIONS
### OF THE $Br_2$-$BrF_3$-$BrF_5$ SYSTEM

| Combination | B.P. 34° C Dark Red Wets Vycor | B.P. 42° C Water White Wets Vycor | B.P. 51° C Dark Red Not Wet Vycor | B.P. 60° C Dark Red Not Wet Vycor | B.P. 127° C Yellow Not Wet Vycor |
|---|---|---|---|---|---|
| $Br_2$ | | | | X | |
| $BrF_5$ | | X | | | |
| $BrF_3$ | | | | | X |
| 4cc $BrF_5$ + 1cc $Br_2$ | X | X | | | |
| 4cc $BrF_5$ + 2cc $Br_2$ | X | | | X | |
| 1cc $BrF_5$ + 4cc $Br_2$ | X | | | X | |
| 4cc $BrF_3$ + 2cc $Br_2$ | | | X | | X |
| 1cc $BrF_3$ + 4cc $Br_2$ | | | X | | X |

at 51° C. The other fraction, found when a dilute solution of $Br_2$ in $BrF_5$ was distilled, was also a dark red liquid which, however, did wet the Vycor surface and boiled at 34° C. Since this fraction was observed in the irradiated liquid it appears again that the predominant decomposition products of $BrF_3$ are $Br_2$ and $BrF_5$.

### B. F/Br Ratios of Low Boiling Fractions

To obtain additional evidence pointing to the identification of $Br_2$ and $BrF_5$, F/Br atomic ratios of the two low boiling fractions were determined. The solutions were analyzed for total bromine and the fluorine was calculated by difference.

The results of the F/Br ratios calculated from these data are compared with F/Br ratios obtained from fractions distilled from synthetic binary mixtures of $Br_2$, $BrF_3$, and $BrF_5$ and are shown in Table II. *

The F/Br ratio for the 34° C boiling fraction agrees fairly well with that of the $Br_2$-$BrF_5$ azeotrope. The F/Br ratio in the case of the colorless liquid boiling at 42° C is probably low since a certain amount of hold-up in the distillation column caused a contamination of this fraction by the 34° C fraction. Nevertheless the values are high enough to again indicate the presence of $BrF_5$.

Thus from the shape of the pressure curves during and after the irradiation, from the striking effect of temperature change on the pressure, from the observation of color and boiling points of the fractions isolated by distillation and from the F/Br ratios of the collected fractions, evidence has been described all pointing to the fact that $Br_2$ and $BrF_5$ are the predominant decomposition products formed during the irradiation of $BrF_3$ by energetic electrons.

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*In the case of the $Br_2$-$BrF_3$ mixtures, the low boiling fraction, boiling at 51° C, was found to have a F/Br ratio of only 0.32. A conversion of this value to weight per cent shows that this fraction contains only about 17% by weight of $BrF_3$. One might suppose that this liquid was merely bromine mechanically contaminated by $BrF_3$ were it not for the fact that the boiling point observed (51° C) was lower than that observed for either $Br_2$, 59° C, or for $BrF_3$, 126° C. In view of the miscibility gap in the $Br_2$-$BrF_3$ system reported by Argonne,[9] the low boiling mixture may well be a vapor phase in equilibrium with two immiscible liquids. An alternate possibility is that the low boiling mixture is an azeotrope.

## TABLE II

### F/Br RATIOS OF FRACTIONS DISTILLED FROM IRRADIATED BrF$_3$

|  |  | Wt. of Sample, gms. | Wt. of Bromine, gms. | % Bromine | F/Br* |
|---|---|---|---|---|---|
|  | BrF$_3$ theoretical |  |  | 58.4 | 3.00 |
|  | BrF$_3$ observed | 9.07 | 5.17 | 57.0 | 3.16 |
|  | BrF$_5$ theoretical |  |  | 45.7 | 5.00 |
|  | BrF$_5$ observed | 1.69 | 0.72 | 42.6 | 5.66 |
|  | Br$_2$-BrF$_5$ "azeotrope" | 6.80 | 4.20 | 61.7 | 2.61 |
|  | Br$_2$-BrF$_3$ "azeotrope" | 5.20 | 4.83 | 93. | 0.322 |
| Fractions From Run #12 | B.P. = 34° C | 0.38 | 0.22 | 58. | 2.9 |
|  | B.P. = 42° C | 0.69 | 0.35 | 51. | 4.4 |
|  | Pot | 7.41 | 4.12 | 55.6 | 3.35 |
| Fractions From Run #14 | B.P. = 34° C | 0.53 | 0.33 | 62. | 2.7 |
|  | B.P. = 42° C | 0.44 | 0.24 | 54. | 3.7 |
|  | B.P. = 127° C | 7.66 | 4.32 | 56.3 | 3.26 |
|  | Pot | 2.65 | 1.52 | 57.3 | 3.14 |

*The fluorine was calculated as the difference between the sample weight and the weight of total bromine.

## V. RESULTS—EXTENT OF DECOMPOSITION

### A. Determination by Distillation Method

To determine the fraction of $BrF_3$ decomposed, the distillation method, used to identify the decomposition products, was first used. The various fractions were collected with the apparatus of Fig. 4, "hydrolyzed" and analyzed for total bromine. The fraction of $BrF_3$ destroyed was calculated by comparing the total bromine content of the low boiling fractions with that of the total sample. In two irradiations a value was also obtained by comparing the weight of the low boiling fractions with the total weight. The results are shown in Table III.

### B. Determination by Spectrophotometric Method

Since only 5 ml $BrF_3$ was available for the fractional distillation and since at most only about 10% of this or 0.5 ml of the $BrF_3$ was decomposed, it was difficult to distill over all the light fractions free of $BrF_3$. This problem became more serious in experiments in which 5% or less of the $BrF_3$ was decomposed. In order to avoid this problem an alternate method of determining the decomposition was carried out, namely, a colormetric determination of free bromine formed by the irradiation with the assumption that the over-all decomposition reaction was:

$$5BrF_3 \longrightarrow Br_2 + 3BrF_5$$
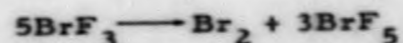
The optical densities of the irradiated liquid were measured with a Beckman Model D.U. spectrophotometer at various wave lengths. A typical absorption curve of an irradiated solution is shown in Fig. 8. The shape of the curve* appears to be identical to that of the synthetic $Br_2$-$BrF_3$ mixtures (see Fig. 9). By comparing the optical densities with those shown in Fig. 10, a $Br_2$ concentration was obtained. The results of $Br_2$ determination for several irradiations appear in Table IV.

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*This curve was obtained 24 hours after the irradiation. A curve measured within 1 hour after the irradiation was displaced upward by a small constant amount. This displacement was attributed to a certain amount of turbidity caused probably by a suspension of insoluble fluorides. In one experiment, the $BrF_3$ was stirred after the setting period and the curve obtained was identical to that taken 1 hour after the irradiation.

## TABLE III

### PER CENT BrF$_3$ DECOMPOSED BY IRRADIATION

(Determined by Fractionation)

| No. of Run | Current μ-amp | Dosage μ-amphr | Fraction Isolated | Wt. of Fraction, g | % BrF$_3$ Decomp. | Total Br, g | % BrF$_3$ Decomp. |
|---|---|---|---|---|---|---|---|
| 10* | 20 | 50.3 | B.P. = 34°C + B.P. = 42°C | | | 0.56 | |
| | | | B.P. = 127°C | | | 4.76} | |
| | | | Pot | | | 0.90} 5.66 | 9.0 |
| 11 | 25 | 34.0 | B.P. = 34°C + B.P. = 42°C | | | 0.56 | |
| | | | B.P. = 127°C | | | 5.11} | |
| | | | Pot | | | 0.42} 5.53 | 9.2 |
| 12 | 25 | 100.0 | B.P. = 34°C | 0.38} | | 0.22} | |
| | | | B.P. = 42°C | 0.69} 1.07 | | 0.35} 0.57 | |
| | | | B.P. = 127°C + Pot | 7.41 | 12.6 | 4.12 | 12.1 |
| 14 | 25 | 84.5 | B.P. = 34°C | 0.53} | | 0.33} | |
| | | | B.P. = 42°C | 0.44} 0.97 | | 0.24} 0.57 | |
| | | | B.P. = 127°C | 7.66} | | 4.32} | |
| | | | Pot | 2.65} 10.31 | 8.6 | 1.52} 5.84 | 8.9 |
| 15* | 5 | 4.0 | B.P. = 34°C + B.P. = 42°C | | | 0.23 | |
| | | | B.P. = 127°C | | | 4.20} | |
| | | | Pot | | | 1.37} 5.57 | 4.0 |

*Samples not weighed.
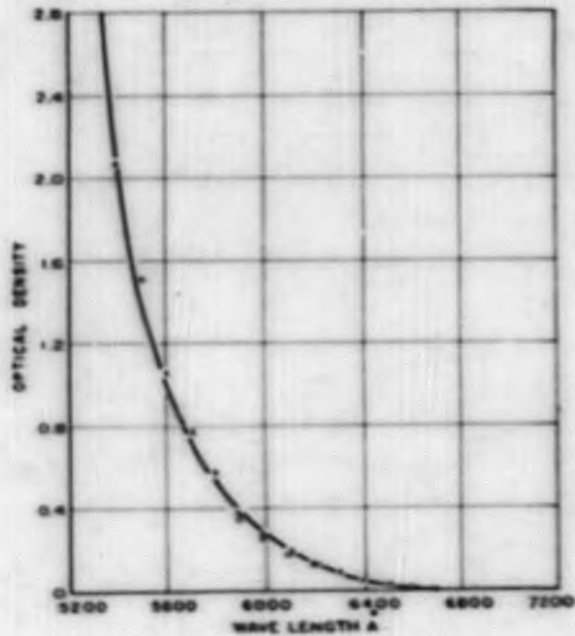
Fig. 8. Absorption Curve of $BrF_3$ Irradiated for 1 hour with a 5-Microampere Beam



| Gms $Br_2$ / 100 ml |
| --- |
| A = 0 |
| B = 0.15 |
| C = 0.30 |
| D = 0.60 |
| E = 0.90 |
| F = 1.65 |
| G = 3.60 |
| H = 8.70 |
| I = 14.1 |
| J = 18.6 |
| K = 27.3 |
| L = 37.2 |
| M = 50.1 |
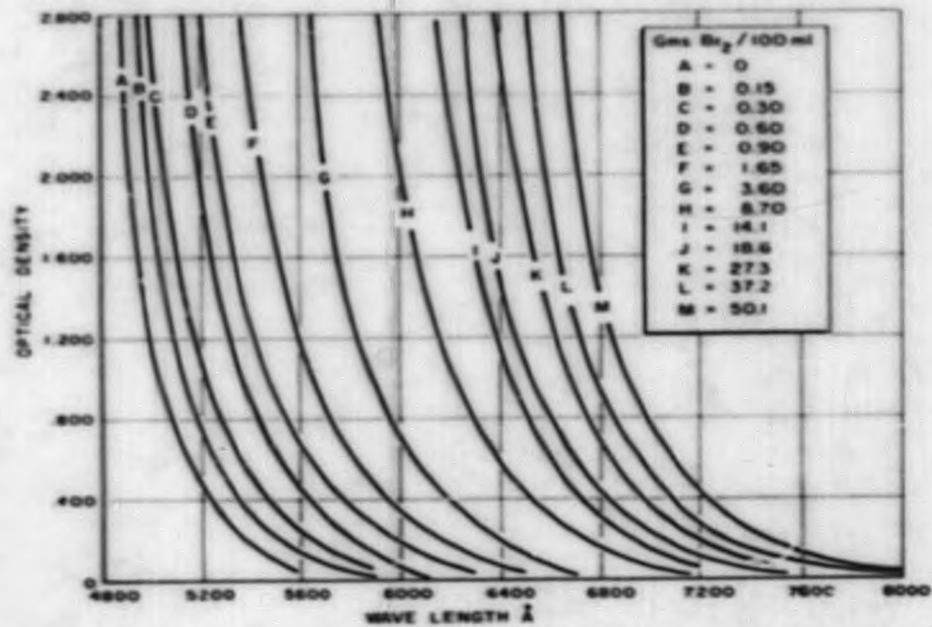
Fig. 9. Optical Densities of $Br_2$-$BrF_3$ System
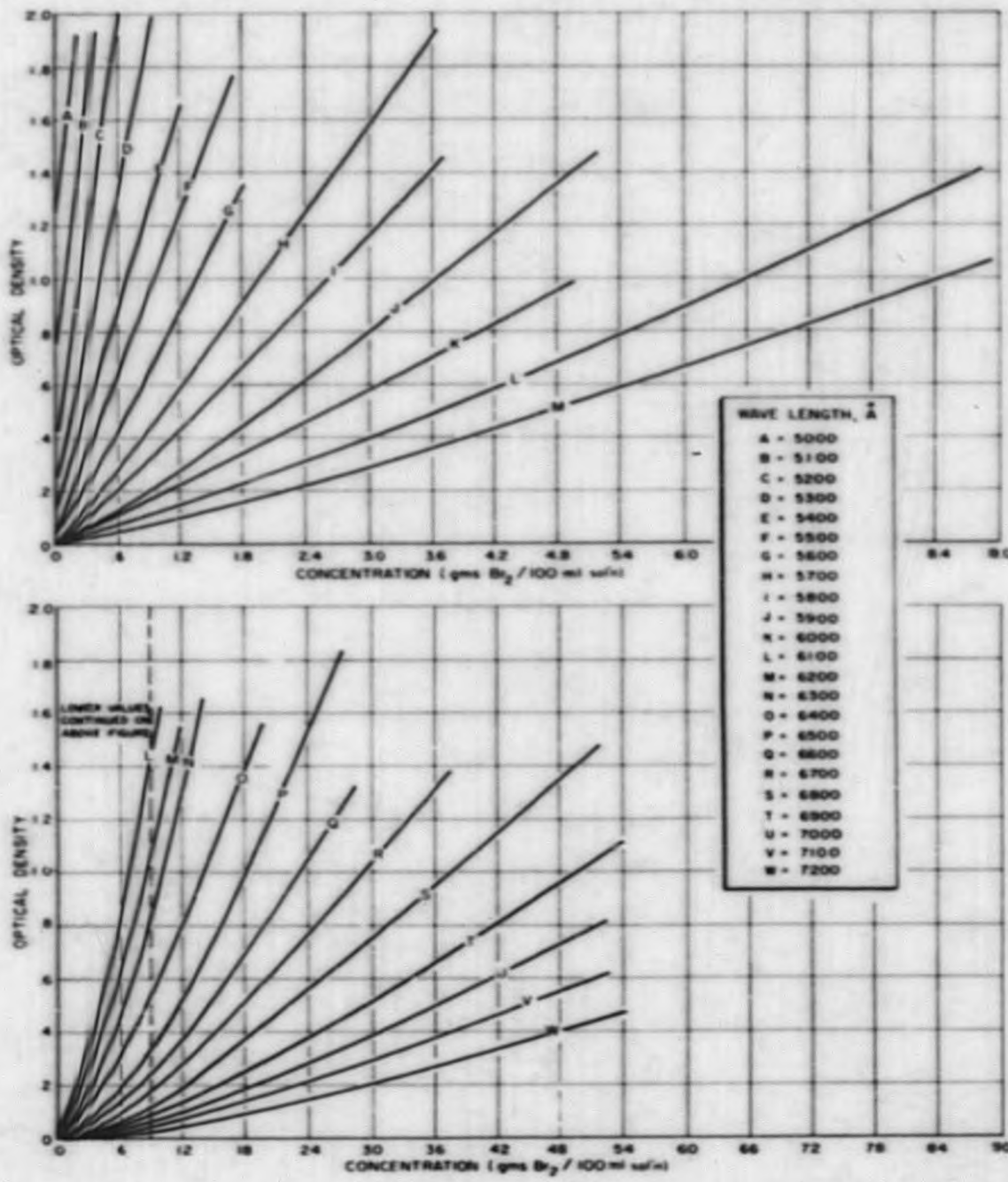
Fig. 10. Optical Density vs Concentration of $Br_2$ in $BrF_3$ for Various Wave Lengths

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## TABLE IV

### FREE BROMINE DETERMINATION OF IRRADIATED BrF₃

| Run No. | Current $\mu$-amp | Dosage $\mu$-amphrs | Wt. % Br₂ |
|---------|------------------|---------------------|-----------|
| 12 | 25 | 100. | 2.4 |
| 14 | 25 | 84.5 | 2.6 |
| 15 | 5 | 7.7 | 0.74 |
| 16 | 5 | 5.0 | 0.58 |
| 17 | 5 | 5.0 | 0.25 |

### C. Comparison of Results of Both Methods

To ensure that the extent of damage of the $BrF_3$ could be calculated from the $Br_2$ results according to the equation,

$$5BrF_3 \longrightarrow Br_2 + 3BrF_5$$
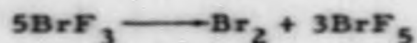
three irradiated samples were analyzed for free bromine with the spectrophotometer and for total bromine by the fractional distillation method. The results are shown in Table V.

## TABLE V

### COMPARISON OF % DECOMPOSITION BY SPECTROPHOTOMETER METHOD AND FRACTIONAL DISTILLATION METHOD

| Run No. | Dosage $\mu$-amphrs | Wt. % Free Br₂ g Br₂/100 g Soln. | % BrF₃ Decomp. (Calc. from Br₂) | % BrF₃ Decomp. (by Fractionation) |
|---------|---------------------|----------------------------------|--------------------------------|-----------------------------------|
| 12 | 100.0 | 2.4 | 9.9 | 12.3 |
| 14 | 84.5 | 2.6 | 10.8 | 8.8 |
| 15 | 7.7 | 0.7 | 3.2 | 4.0 |

The agreement between the observed decomposition and that calculated on the basis of free bromine is sufficiently satisfactory to permit the assumption that the reaction mentioned above is the over-all reaction. It is felt that the spectrophotometric method was more accurate since the small volume of $BrF_3$, as discussed previously, leads to considerable error when the distillation method is used. For this reason the spectrophotometric value was chosen whenever available.

## D. Extent of Decomposition vs Dosage

The extent of $BrF_3$ decomposition based on the free bromine content was calculated for several samples and the results are shown in Fig. 11. The values of two runs, for which only the distillation method was carried out is also included. As in the pressure curves it appears that a steady state is being approached.

An equation of the form:

$$Y = Y_\infty (1 - e^{-KD}) \qquad \qquad \dots (5)$$

was assumed where $Y$ = the fraction of $BrF_3$ decomposed at the dosage D in microampere hours. $Y_\infty$ is the steady state fraction of $BrF_3$ destroyed and K is a constant. A glance at Fig. 9 suggests that a value of 0.105 seems reasonable for $Y_\infty$. By using the value of $Y = 0.024$ for $D = 5$ microampere hours, the following equation was obtained:

$$Y = 0.105 (1 - e^{-.0518D}) \qquad \qquad \dots (6)$$

The curve drawn in Fig. 9 represents this equation and applies to an irradiation of 5 cc $BrF_3$.

## E. Calculation of $D_{1/2}$

The half exposure, $D_{1/2}$, required for the decomposition to reach a concentration of half the saturated value was calculated from Eq. 6 by letting $\frac{Y}{Y_\infty}$ = 1/2 and was found to be 13.3 microampere hours.

## F. Calculation of "G" Value

A "G" value, the number of molecules decomposed by 100 ev, was calculated at zero dosage in order to eliminate the back reaction effects. For this calculation it was necessary to know both the energy in ev produced per microampere hour and the number of molecules of $BrF_3$ destroyed per microampere
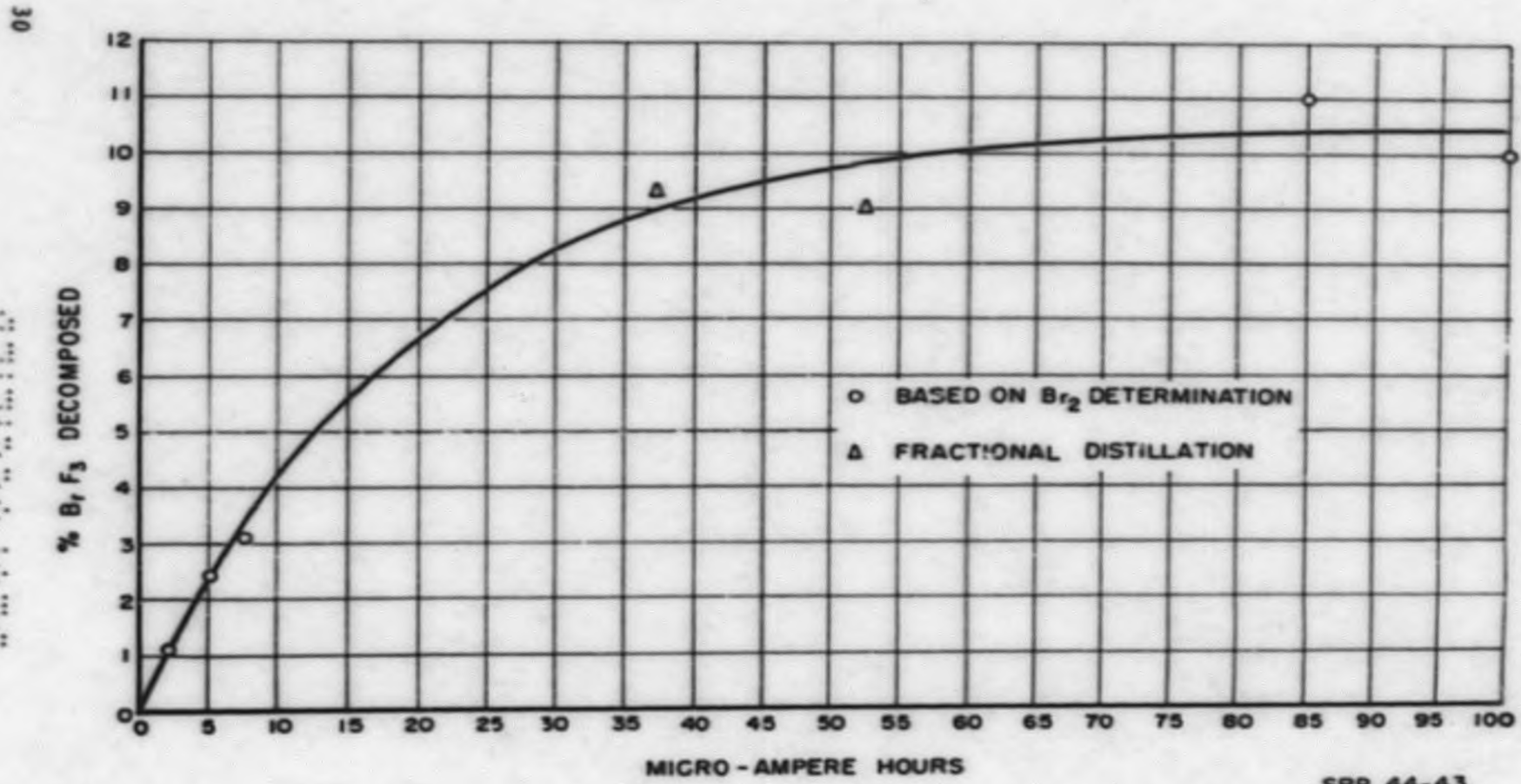
Fig. 11. Per Cent BrF$_3$ Decomposed by Electron Irradiation

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hour. The energy of a microampere hour of 1-Mev electrons is equivalent to

$$\frac{10^{-6} \text{ amp}}{\text{microamp}} \times 3.6 \times 10^3 \frac{\text{sec}}{\text{hour}} \times 10^6 \text{ ev/electron}$$

$$= 3.6 \times 10^{-3} \frac{\text{coulomb}}{\text{microamp hr}} \times 10^6 \text{ ev/electron}$$

$$= \frac{3.6 \times 10^{-3}}{1.6 \times 10^{-19}} \frac{\text{coulomb/microamp hour}}{\text{coulomb/electron}} \times 10^6 \text{ ev/electron}$$

$$= 2.2 \times 10^{22} \text{ ev/microampere hour}$$

The fraction, Y, of $BrF_3$ destroyed per microampere hour, D, was found by differentiating Eq. 5

$$\frac{dY}{dD} = K Y_{\infty} e^{-K D} \qquad \qquad \text{. . . (7)}$$

At zero dosage $\left(\frac{dY}{dD}\right)_o = K Y_{\infty} = 0.0055/\text{microampere hour}$. Since 5 cc (6.2 $\times 10^{22}$ molecules) $BrF_3$ were originally present, $0.0055 \times 6.2 \times 10^{22}$ or 3.4 $\times 10^{20}$ molecules of $BrF_3$ are decomposed by the beam per microampere hour. Thus

$$\frac{3.4 \times 10^{20} \text{ molecules/microampere hour}}{2.2 \times 10^{22} \text{ ev/microampere hour}} \quad \text{or } 1.5 \times 10^{-2}$$

molecules/ev is equivalent to a "G" value of 1.5.

## VI. GENERAL DISCUSSION OF RESULTS

### A. Mechanism

Although this study was not sufficiently extensive to allow a detailed mechanism to be postulated, certain general features of the mechanism can be deduced. The form of decomposition versus irradiation curve, Eq. (5), will be shown to be that expected if the rate of the forward reaction (8) and reverse reactions (10, 11) are all first order and are proportional to the beam intensity, I.

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$$BrF_3 \xrightarrow{k_1} products \ (a) \qquad \qquad \ldots (8)$$

$$products \ (a) \xrightarrow{fast} Br_2 + BrF_5 \qquad \qquad \ldots (9)$$

$$Br_2 \xrightarrow{k_2} products \ (b) \qquad \qquad \ldots (10)$$

$$BrF_5 \xrightarrow{k_3} products \ (c) \qquad \qquad \ldots (11)$$

$$products \ (b) + products \ (c) \xrightarrow{fast} BrF_3 \qquad \qquad \ldots (12)$$
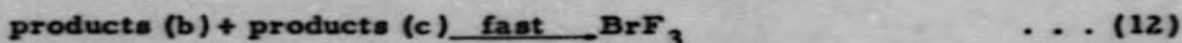
The over-all reaction for the decomposition of $BrF_3$ may be written

$$5BrF_3 \longrightarrow Br_2 + 3BrF_5 \qquad \qquad \ldots (13)$$

If out of "a" moles of $BrF_3$, x moles of $Br_2$ and 3x moles of $BrF_5$ are formed after D microampere hours of irradiation, then $\frac{x}{a}$ is the concentration of $Br_2$, $\frac{3x}{a}$ is the concentration of $BrF_5$ and $\frac{a-5x}{a}$ is the concentration of $BrF_3$.*

The rate of formation of $Br_2$ or $\frac{d\frac{x}{a}}{dt}$ is given by

$$\frac{d\frac{x}{a}}{dt} = k_1 \ I \left( \frac{a-5x}{a} \right) - k_2 \ I \frac{x}{a} - 3k_3 \ I \frac{x}{a} \qquad \qquad \ldots (14)$$

$$\frac{dx}{dt} = I \left[ k_1 (a - 5x) - k_4 x \right] \qquad \qquad \ldots (15)$$

where $k_4 = k_2 + k_3$. Integrating:

$$x = \frac{k_1 a}{5 k_1 + k_4} \left[ 1 - e^{-(5 k_1 + k_4)It} \right] \qquad \qquad \ldots (16)$$

Since at $t = \infty$, $x = x_\infty$:

$$\frac{5x}{a} = \frac{5x_\infty}{a} \left[ 1 - e^{-\frac{ak_1 It}{x_\infty}} \right] \qquad \qquad \ldots (17)$$

---

*Actually $\frac{x}{a-x}$, $\frac{3x}{a-x}$, and $\frac{a-5x}{a-x}$ are the true concentrations. Since x in this case is small compared to "a", the terms described above are used in order to simplify the calculations.

Since It = D, this had the form of Eq. 5 where

$$\frac{5x}{a} = Y, \quad \frac{5x_{\infty}}{a} = Y_{\infty} \quad \text{and } k_1 = \frac{Y_{\infty} K}{5}$$

Using the values of $Y_{\infty}$ = 0.105 and K = 0.0518, $k_1$ = 0.00109/microampere hour, $k_4 = k_1 \left( \frac{a - 5x_{\infty}}{x_{\infty}} \right)$ = 42.7 $k_1$. From this result it appears that $Br_2$ and $BrF_5$ are affected by the irradiation to a considerably greater extent than is $BrF_3$. That is, the reverse reactions are intrinsically more rapid than the decomposition of $BrF_3$. This result was to be expected from the relatively small value of $Y_{\infty}$.

The above treatment applies to 5 cc $BrF_3$ only. For a more general expression the dosage, D, should be replaced by a "dosage density, D' which is expressed in microampere hours/cc $BrF_3$. For this case:

$Y_{\infty}$ remains 0.105
$D_{1/2}$ becomes 2.7 microampere hours/cc
K = 0.259 cc/microampere hour

Thus Eq. (6) becomes

$$Y = 0.105 \, (1 - e^{-.259 \, D'})$$
$$k_1 = 0.00545 \text{ cc/microampere hour}$$
and $k_4$ remains 42.7 $k_1$

Additional information in the form of thermodynamic and spectroscopic data of the bromine-fluorine system is required before the most reasonable detailed mechanism leading to the formation of $Br_2$ and $BrF_5$ can be postulated.

B. Comparison of Irradiation Dosages from Statitron with Those Expected from Spent Fuels

In order to relate the experimental results obtained with the possible engineering use of $BrF_3$ for spent fuels it is necessary to evaluate the Statitron dosages in terms of those expected from the fuels. Three types of irradiated fuel will be considered.

1. Hanford fuel (flux ~$10^{13}$ n/cm$^2$/sec) which has been in the reactor for 100 days.

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2. Enriched type fuel (flux $\sim 10^{13}$ $n/cm^2/sec$) which has been in the pile for 100 days.

3. MTR type fuel (flux $\sim 10^{14}$ $n/cm^2/sec$) which has been in the pile for 12 days.

It will first be shown that the intensity of electrons produced by the Statitron exceeds that expected from most of the above fuels. The number of electrons/sec corresponding to a microampere ($10^{-6}$ coulombs/sec) beam is:

$$\frac{1 \times 10^{-6} \text{ coulombs/sec/microampere}}{1.6 \times 10^{-19} \text{ coulombs/electron}} \text{ or } 6.2 \times 10^{12} \text{ electrons/sec/}$$

microampere. This intensity corresponds to $\frac{6.2 \times 10^{12} e^-/sec/microamp}{3.7 \times 10^{10} e^-/sec/curie}$ or

170 curies/microampere. Thus the samples were irradiated with 170 curies/microampere of electrons produced by the Statitron.

In order to compare this radiation intensity with that expected from actual fuel it is first necessary to know the amount of uranium which is expected to be dissolved by the $BrF_3$. This is not known exactly. In a flow sheet of the Fluoride Volatility Process it was proposed that about 5 grams of $BrF_3$ be used for each gram of uranium.[10] In the experiments discussed in Fig. 9, 5 cc $BrF_3$ (14 grams) was irradiated and therefore the radiation intensity from the Statitron (170 curies/microampere) will be more or less qualitatively compared with that emitted by 3 grams of uranium. The beta activities of the fuels mentioned above were calculated from the curves of Thornton and Houghton[11] and are given in Table VI.

Since the experiments discussed in this report have dealt with irradiations of 5-25 microamperes (850-4250 curies) it is seen that the intensity of electrons produced by the Statitron far exceeds that expected of even 1-day cooled Hanford fuel.* Even if the Hanford fuel is in contact with the $BrF_3$ for as long as 100

---

*Of course during the initial irradiation period, the beta rays will be essentially "self-absorbed" by the undissolved bulk uranium. Thus at this stage the radiation damage to the $BrF_3$ will be due mainly to gamma rays. However, the power emitted by beta rays and gamma rays of burnt $U^{235}$ fuels are comparable.[12]

## TABLE VI

### BETA ACTIVITY EXPECTED FROM 3-GRAMS URANIUM

| Type Fuel | Approx % $U^{235}$ | Flux n/cm$^2$/sec | In Pile Days | Out Pile Days | Activity for 3 g U, curies | Corresp Beam Int Microamps |
|---|---|---|---|---|---|---|
| Hanford | 1 | $10^{13}$ | 100 | 100 | 1.2 | 0.007 |
| Hanford | 1 | $10^{13}$ | 100 | 1 | 9.6 | 0.056 |
| Enriched | 100 | $10^{13}$ | 100 | 100 | 120 | 0.71 |
| Enriched | 100 | $10^{13}$ | 100 | 7 | 512 | 3.0 |
| Enriched | 100 | $10^{13}$ | 100 | 1 | 960 | 5.6 |
| MTR Type | 100 | $10^{14}$ | 12 | 100 | 340 | 2.0 |
| MTR Type | 100 | $10^{14}$ | 12 | 60 | 447 | 2.6 |
| MTR Type | 100 | $10^{14}$ | 12 | 7 | 2700 | 16 |
| MTR Type | 100 | $10^{14}$ | 12 | 1 | 6260 | 37 |

hours (6 microampere hours) only about 2 per cent of the $BrF_3$ would be de-composed. In the case of the 1-day cooled enriched fuel (flux = $10^{13}$ n/cm$^2$/sec) a 20-hour contact would yield approximately 100 microampere hours while in the case of 1-day cooled MTR fuel about 3 hours contact time would yield a 100-microampere hour dosage. However, since there appears to be a saturation effect, one may not need to be too concerned with the dosage given to the $BrF_3$ since the radiative rate of the back reaction of the decomposition products to regenerate $BrF_3$ is sufficiently rapid to keep the decomposition of $BrF_3$ at no greater than approximately 10 per cent. * If the uranium dissolution in $BrF_3$ is carried out at elevated temperatures, as has been proposed, the extent of radi-ation damage may be even less since it has been shown that reaction between

---

*It should be pointed out that while in the case of $BrF_3$ under an irradiation field a steady state exists, such may not be the case when uranium is present. It is possible that free radicals and other intermediates with relatively long lifetimes (up to a few seconds) are formed which are very reactive with the uranium. If such radicals or ions reach the uranium surface before they are altered into a relatively inert form the dissolution of the uranium will be accelerated. Thus an investigation of the radiation effects of the uranium-$BrF_3$ system should be carried out both at room temperature and at elevated temperatures.

$Br_2$ and $BrF_5$ to form $BrF_3$ becomes appreciable at temperatures above 100° C. [4] Thus, from these experiments it would appear that $BrF_3$, from a radiation resistance standpoint, is an excellent reagent for the processing of short cooled fuels.

# APPENDIX A

## CALIBRATION OF STATITRON POWER

To calibrate the Statitron power it was desirable to use a dosimeter with which the calibration could be carried out conveniently and quickly. Such a dosimeter, based on calorimetry is described below.

In order to bypass special techniques required to avoid heat loss which accompanies a high $\Delta T$, a flow type calorimeter was used. In this method water with a constant flow rate is irradiated. By measuring the flow and the difference in temperature of the incoming and outgoing water, the power can be calculated by the equation:

$$P = 4.18 \ Tvs$$

where

> P is the power in watts
>
> 4.18 is the conversion factor from calories to joules
>
> T is the temperature rise in ° C
>
> v is the flow rate of water (cc/sec) and
>
> s is the specific heat of water (1 cal/°cc).

The dosimeter, shown in Fig. A-1 consisted of a hollow brass cell which served as the calorimeter. The temperature rise was measured with a differential iron-constantan thermocouple, which was soldered along the outer edge of short pieces of copper tubing thermally isolated from the rest of the system with Tygon tubing. Although the apparatus was so designed that the water entered at a few degrees below ambient temperature and left a few degrees above thus tending to reduce over-all heat losses or gains to a minimum, the calorimeter was nevertheless wrapped with glass wool. The water flow, measured with a Fisher-Porter flowmeter, was adjusted by means of a pinch clamp. A constant head tank insured constant water pressure.

The values of five determinations carried out at different power levels are shown in Table A-1 The agreement between the Statitron readings and calorimetric values, about 90 per cent in all cases, is considered quite satisfactory.

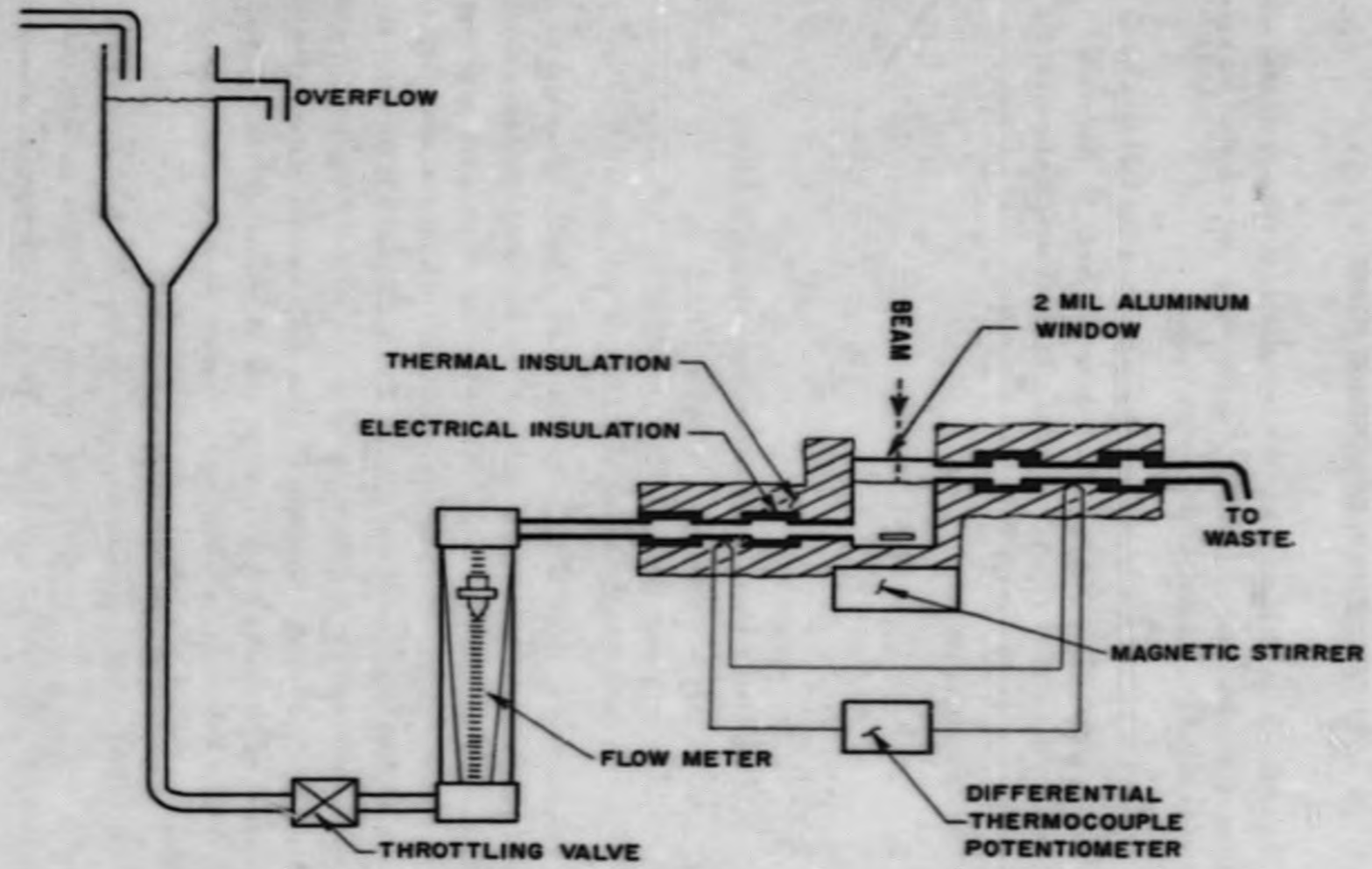OVERFLOW

2 MIL ALUMINUM
WINDOW

THERMAL INSULATION

BEAM

ELECTRICAL INSULATION

TO
WASTE

MAGNETIC STIRRER

FLOW METER

DIFFERENTIAL
THERMOCOUPLE
POTENTIOMETER

THROTTLING VALVE

Fig. A-1.  Flow Calorimeter for Califration of Statitron Power Output

## TABLE A-I

### CALIBRATION OF POWER INSTRUMENTS OF STATITRON

| Statitron Readings, watts | Water Flow, cc/sec | $\Delta T$ °C | Power, cal/sec | Power, watts | Deviation, % |
|---|---|---|---|---|---|
| 5 | 0.250 | 5.4 | 1.35 | 5.6 | -11.5 |
| 10 | 0.225 | 9.8 | 2.20 | 9.2 | 8.8 |
| 15 | 0.220 | 15.0 | 3.31 | 13.8 | 8.7 |
| 20 | 0.210 | 20.2 | 4.25 | 17.8 | 12.5 |
| 25 | 0.210 | 25.2 | 5.30 | 22.2 | 12.5 |

# APPENDIX B
## TESTS FOR SUITABLE ELECTRON BEAM WINDOW

In the designing of the reaction cell, used in the $BrF_3$ irradiations by energetic electrons of the Statitron, consideration had to be given to suitable windows to permit the passage of the beam. The requirements for such windows are:

1. It must be possible to maintain a static vacuum in the cell containing such a window.

2. The window must be strong enough so that rupture, due to a pressure increase in the cell, will not be likely.

3. The material of the window and gasket must be such that corrosion by $BrF_3$ is kept to a minimum.

4. The window must be sufficiently thin to avoid any appreciable decrease in energy and intensity of the incident electrons.

Since 2S aluminum is known to be rather inert to $BrF_3$, experiments which are discussed below were performed to determine if this substance met the above requirements for a suitable window. Two types of aluminum windows were under consideration:

1. A thin foil of 1 to 2 mil thickness sandwiched between 2 thin Teflon gaskets.

2. A thin machined window.

Among the advantages of the first type of window would be ease of fabrication. Thus after each run this window could be easily replaced. Further, the thickness of such a window could be as low as 1 mil while 3 mils is probably the limit of the thickness of the machined window.

To test the foil window, a 1/16-inch thick Teflon gasket was placed on an aluminum test cell which had a cylindrical opening of 5/8-inch diameter. A 1- or 2-mil aluminum foil was set on the gasket. A brass disc with the same size opening in the center was placed over the foil and the entire system clamped tight. The system was tested with a Consolidated Mass Spectrometer Type Helium Leak Detector and no leak could be detected.

The bursting pressures of the foil were then determined by pressurizing the vessel. For the 1-mil foils the bursting pressures were 29, 34, and 32 psi gauge pressures. Tests for three of the 2-mil foils revealed that these windows did not blow at 50 psi. It was conceivable that hot $BrF_3$ vapors might sufficiently corrode the thin aluminum to lower the bursting pressure. To check this possibility, about 1 cc $BrF_3$ was introduced into the cell and the window was secured. The cell was then heated for about 1 hour at a gauge pressure of 15 psi $BrF_3$ vapor. Thus the temperature of the $BrF_3$ vapor was approximately its boiling point (126° C). At the end of the heating time, the cell was cooled and the window removed. A visual inspection revealed no pits in the foil. The bursting pressure of two 1-mil foils treated in this manner were both 31 psi. To submit the aluminum to even harsher conditions, a 1-mil aluminum foil was immersed for 1 hour into liquid boiling $BrF_3$. At the end of this period the foil was mounted on the cell. The bursting pressure of the foil was 34 psi. Thus it appeared that corrosion of the window would not present a problem.

Since the range of 1-Mev electrons in aluminum is about 60 mils, a window of 1-mil thickness should not decrease either the energy or intensity of the electron beam to any considerable extent.

With these satisfactory results, a 1-2 mil aluminum foil was selected for the cell window.

# APPENDIX C

## TOTAL BROMINE ANALYSIS OF BrF$_3$ AND BrF$_5$

In order to confirm the identity of $Br_2$ and $BrF_5$ as decomposition products and to determine the extent of decomposition of $BrF_3$ by the radiation field it was desirable to analyze the irradiated $BrF_3$ for total bromine. In order to do this by chemical methods, it was necessary to convert the irradiated liquid into a more inert form. One method which was developed at the Argonne National Laboratory[13] involves the use of a thermally sealed Fluorothene bag which includes the frozen sample. Water or a saturated aqueous solution of aluminum nitrate is then cautiously injected through the bag into the sample. One disadvantage of this method is the violent and therefore hazardous reaction of $BrF_3$ with aqueous solutions. To eliminate this hazard the bag technique has been modified by allowing the $BrF_3$ to drip into anhydrous sodium carbonate. The reaction is smooth and is not accompanied by flame or "popping". The bag is shown in Fig. C-1 A brass clamp seals the entry portion of the bag thus avoiding a thermal seal. A Vycor collection tube, containing the frozen sample is clamped with a Teflon holder into such a position that as the sample melts, it enters dropwise through the side arm into a beaker containing the anhydrous sodium carbonate. This beaker is clamped into position with a Fluorothene holder. Since the reaction liberates bromine and carbon dioxide among other products, a saturated solution of sodium hydroxide contained in a beaker is used to absorb these gases. As more bromine and carbon dioxide are generated, the clamp is loosened manually and the beaker upset to produce a greater area of the absorbing solution. When the collection tube is empty, the solution is gently swirled until all the bromine vapors are absorbed. The sodium carbonate is then upset to permit the sodium hydroxide solution to react with the last traces of $BrF_3$. The clamp is then loosened and the solution removed. The bromine in its various states was reduced to bromide with $SO_2$ and titrated with $AgNO_3$ using $K_2CrO_4$ as an indicator.

The procedure was checked by analyzing samples of $Br_2$, $BrF_3$, and $BrF_5$ in the above manner. The results are given in Table IV. The agreement appears quite good in the case of $Br_2$ and $BrF_3$. In the one case of $BrF_5$, while deviation was larger, agreement was still sufficiently good to warrant this method for the analysis of the irradiated solutions.
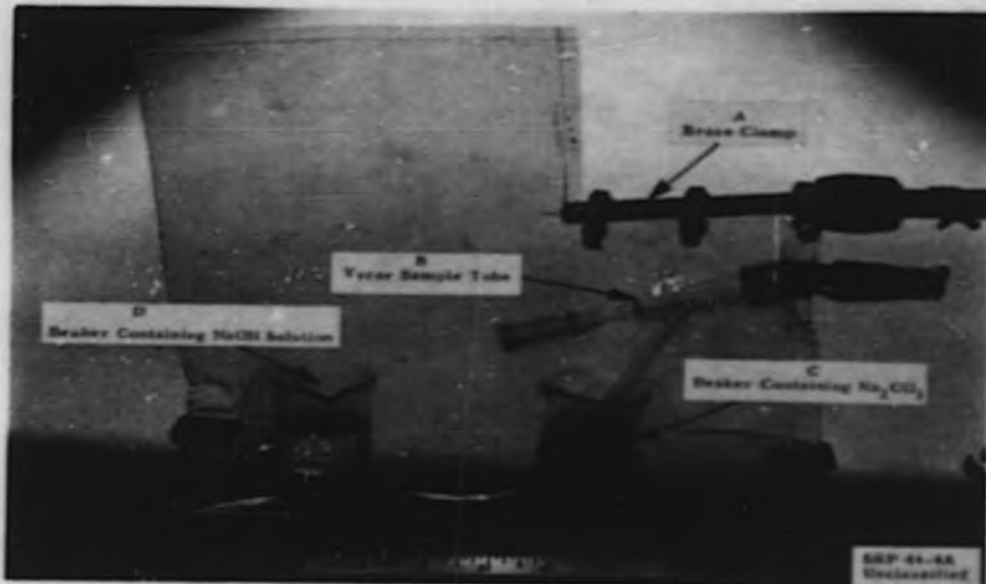
Fig. C-1.   Modified Fluorothene Bag for "Inactivating" $BrF_3$

## TABLE C-I

### TOTAL BROMINE ANALYSES OF $Br_2$, $BrF_3$, AND

### $BrF_5$ FOLLOWING $Na_2CO_3$-NaOH REACTION

|  | Sample Wt., g | Total Bromine, g | Theoretical Wt. of Bromine, g | Per Cent Deviation |
|---|---|---|---|---|
| $Br_2$ | 12.45 | 12.45 | 12.80 | 2.7 |
| $BrF_3$ | 8.69 | 4.93 | 5.06 | 2.6 |
| $BrF_3$ (purified by distill) | 9.07 | 5.17 | 5.30 | 2.4 |
| $BrF_5$ (purified by distill) | 1.69 | .72 | .77 | 6.5 |

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