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AN INVESTIGATION OF A METHOD OF PREPARATION OF BORON TRIFLUORIDE FROM COLEMANITE ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)

II AN INFRA-RED STUDY

A Thesis

Presented to

the Faculty of the Department of Chemistry

Appalachian State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

William Marcus Cooke

June, 1969

AN INVESTIGATION OF A METHOD OF PREPARATION OF

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INTRODUCTION

In an earlier investigation[12] the preparation of boron trifluoride, BF_3, via the reaction of sulfuric anhydride, SO_3, with a mixture of calcium fluoride, CaF_2 (fluorspar), and the boron mineral, Colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$), was found to be feasible. The present study extends the previous investigation to include further study of the reaction parameters in an effort (1) to increase boron trifluoride yield, (2) to identify the gaseous reaction products, and (3) to isolate boron trifluoride from the reaction system.

In the earlier portion of this continuing investigation[10] the boron trifluoride was assayed by hydrolysis in sodium hydroxide solution, followed by determination of the boron in solution by the conventional analytical procedure[3]. Since an ultimate purpose of the investigation was the recovery of the boron, as boron trifluoride, attention was given to non-destructive analytical methods and isolation of the product from the reaction mixture.

While recovery of the boron trifluoride from the gas stream, by fractional condensation in a closed system, probably represents the most desired method of recovery, the limited availability of coolants - liquid nitrogen and dry ice - precluded investigation by this procedure.

The availability of infra-red instrumentation, also the belief that the gaseous reaction product would be infra-red sensitive, focused attention on this method, from a qualitative and possibly a quantitative standpoint. A search of the literature revealed the

presence of ample spectral data for the proposed gaseous reaction products[1,2,4-7,9-11] and thereby infra-red analysis was selected. The infra-red and alkaline hydrolysis determination on separate portions of a typical gaseous product mixture was taken as proof of the acceptability of the infra-red method.

As an alternative to the direct recovery of boron trifluoride, conversion to the diethyl etherate, for which ample physical data were available[8], and subsequent isolation of the etherate adduct also constituted a part of this investigation. Coincidentally, the infra-red identification and measured physical properties of the etherate adduct substantiates the contention that the volatilized boron is present, in the gaseous reaction products, as boron trifluoride.

MATERIALS AND EQUIPMENT

The Colemanite used in this investigation was furnished by the U. S. Borax and Chemical Company representing material from Turkish deposits. Stated analysis, 42.18% B_2O_3, corresponds to approximately 83% purity of the mineral sample.

The calcium fluoride, CaF_2, was Matheson, Coleman and Bell Fluorspar (Native Powder).

The sulfur trioxide was Baker and Adamson (Sulfan) stabilized of minimum purity 99.5%.

Materials used in the moisture analysis - Karl Fischer Method - were obtained from the Fischer Scientific Company.

Other chemicals and materials used were of ACS standard purity and were obtained from scientific supply houses.

The reaction vessel was a Parr Instrument Company Series 4500 Pressure Reaction Apparatus including the internal stirrer and heating unit. In order to prolong the life of the apparatus and to insure safer operating conditions, the silver rupture disc was replaced by a gold disc and the stirrer removed. The entry port for the stirrer was plugged with a Teflon plug to prevent gas loss and also to reduce corrosion.

The gaseous samples were analyzed with a Beckman IR-7 Infra-Red Spectrophotometer. Liquid samples associated with the boron trifluoride etherate portion of the investigation were analyzed with a Perkin-Elmer Model 137B Infracord Spectrophotometer.

The infra-red gas cell, path length 9.0 cm, had calcium fluoride optical windows and was obtained from the Isomet Corporation, Palisades

Park, New Jersey. Calcium fluoride windows were chosen over the customarily used sodium chloride windows in an effort to reduce reaction with components of the gaseous reaction product mixture.

The cell employed in the analysis of liquid samples was of the demountable type with standard sodium chloride windows.

EXPERIMENTAL

Determination and Removal of Water

Confirmation of the removal of water from the "as received" Colemanite by ordinary drying techniques, at about 430°C, was carried out employing Karl Fischer techniques. (Prior removal of water reduces the loss of product via the hydrolysis of boron trifluoride.)

The Karl Fischer reagent was standardized against sodium tartrate dihydrate and found to have a titer of 4.42 mg H_2O/ml reagent. Several samples of Colemanite, dried at 430°C for four hours, were analyzed and found to have a water content equivalent to 1.19 mg/g of dried sample. This was deemed to represent sufficient water removal so as not to influence subsequent reactions. As previously noted[12] the drying of Colemanite at temperatures above 400°-450°C causes loss of material through some unexplained fuming process.

Boron Analysis

In the course of this investigation Colemanite samples, solid reaction residues, hydrolyzed gaseous products, and etherate samples were analyzed for boron content by the method of the Pacific Coast Borax Company[3] except that a pH meter was used to adjust the solutions to the methyl red end-point prior to titration in order to improve the subsequent phenolphthalein end-point. (The use of the pH meter was checked against the original procedure on simultaneous Colemanite analyses.)

In this procedure the boron containing sample is solubilized by treatment with hydrochloric acid in order to decompose any borate remaining. The pH of the solution is then adjusted to the methyl red end-point with sodium hydroxide and a few drops of saturated bromine water is added to oxidize ferrous iron. After boiling to remove excess bromine, barium carbonate is added and the solution again brought to a boil. To prevent precipitation of barium borate, the total volume, of solution, is adjusted to 100 ml for each estimated 0.5 gm B_2O_3 present. After again heating, the solution is allowed to stand for at least an hour after which the insoluble solids are filtered off and washed with water. The combined filtrate and washings are acidified with hydrochloric acid and boiled to remove dissolved carbon dioxide after which the pH is again adjusted to the methyl red end-point with sodium hydroxide solution. Mannitol is then added to complex the boric acid and the solution is titrated to the phenolphthalein end-point with standard sodium hydroxide.

By this method the B_2O_3 content of the Colemanite used in this study was 50.5% (77.7% pure) based on the furnace dried material.

Reaction Procedure

The conditions employed in the Colemanite - CaF_2 - SO_3 reactions were the same as previously described in the earlier part of this investigation and are repeated herein primarily for purposes of clarification to the reader, with exceptions noted where necessary.

In this procedure weighed samples of the dried solid reactants - Colemanite and calcium fluoride - are thoroughly blended by rotation in a closed sealed jar for 15 minutes or more, after which they are quantitatively transferred to the reaction vessel. The reaction vessel head is then secured to the reactor and a vacuum carefully drawn. In evacuating the reactor it is imperative that the vacuum be slowly applied, and that it be applied from the valve which does not extend below the reaction vessel head so as to minimize loss of the powdery reaction mixture. This can be conveniently done after the dropping funnel is attached, permitting a check on the tightness of the connection between the reactor and the funnel. The sulfur trioxide is then drawn into the reactor by opening the appropriate valve. The weight of the sulfur trioxide used is determined by weight differenc of the stock bottle. The reactor is then heated to the specified temperature and held there for the desired period of time during which reaction was assumed to occur.

Except for those portions taken for infra-red analysis or used in the preparation of the etherate adduct, the gaseous reaction

products were slowly passed into a scrub train consisting of three one-quart polyethylene bottles, connected in series, containing sodium hydroxide solution. When the pressure within the reactor came to atmospheric, a gentle stream of dry nitrogen was passed through the system for about three hours to insure complete removal of the gaseous reaction products. Nitrogen was admitted to the system through the same valve through which the sulfur trioxide was added. The contents of the scrub train were then analyzed as previously described.

Solid reaction products were removed from the bottom of the reactor and also analyzed for the residual boron content. The consistency of these products varied from a loose powdery form to a homogeneously hard mass. The reason for these conditions is not known.

Where samples of the gas mixture were taken for infra-red analysis, the infra-red cell was connected into the system between the reactor and the first bottle of the scrub train. Drying tubes were inserted both before and after the cell in order to maintain conditions as anhydrous as possible. The system was then reduced to atmospheric pressure through this modified system insuring the maximum possible gas concentration in the cell. The sample cell was then closed off, removed from the system, and the reactor flushed in the usual manner with dry nitrogen. Where conditions warranted lesser concentration of gas, dry nitrogen was passed through the cell while connected into the scrubbing system.

In the preparation of $BF_3 \cdot Et_2O$ gaseous boron trifluoride is

passed into diethyl ether. In those reactions where the etherate adduct was the desired product, an absorption train was substituted for the previously described scrub train. This consisted of (1) a 250 ml flask as a ballast, (2) three 300 ml tall form gas-drying bottles with fritted glass dispersers, containing diethyl ether, and (3) a water-cooled condenser and receiver at the exit end to minimize ether loss. The ether from the various parts of the absorption train was combined and the unreacted ether distilled off in a 250 ml distillation apparatus, until about 100 ml of liquid remained. The remaining liquid was then quantitatively transferred to a "Mini-Lab" fractional distillation apparatus for separation and determination of boiling points, of the various fractions. Those fractions boiling above the boiling point of the ether were infra-red analyzed employing a capillary liquid cell.

DISCUSSION OF RESULTS

The investigation of the Colemanite -CaF_2-SO_3 reaction system was initially undertaken on the basis of thermodynamic calculations which indicated a sufficiently large negative free energy for the reaction, proceeding to formation of boron trifluoride and calcium sulfate. It is to be noted that exact thermodynamic data are not available for Colemanite; however, comparison of data available for related minerals, from which data for Colemanite were estimated, indicated the desired reactions to be favored. Subsequently this contention was verified by actual experiment.

Calculations and experiments were based upon the stoichiometry shown in the following reaction:

$$2CaO \cdot 3B_2O_3 + 9CaF_2 + 11SO_3 \longrightarrow 6BF_3 + 11CaSO_4$$

In this study a number of experiments, of which a total of ten are described, were carried out varying reaction conditions to obtain products for analysis and/or further study.

The first three experiments, data for which are shown in Table I, were carried out, prior to the acquisition of the infra-red gas cell, for the purpose of verifying the observation that heating time did not influence product yield and to provide familiarization with techniques involved in reaction procedures. (It is to be noted that sulfur trioxide is an extremely reactive substance requiring utmost caution and care in handling.) In reactions 2, 3, and 4, heating times were varied 3, 1.5, and 6 hours respectively. Analysis of the data indicates that, within experimental error, variation in heating

TABLE I

THE COLEMANITE - CaF_2-SO_3 SYSTEM: MOLAR RELATIONSHIPS AND PRODUCT ANALYSIS

Reaction Number	Moles			Molar Ratio	% B_2O_3
	Colemanite(1)	CaF_2	SO_3	Colemanite /CaF_2/SO_3	Accounted for
1	0.836	0.650	1.84	1 : 7.78 : 22.0	81.1
2	0.0726	0.697	0.838	1 : 9.60 : 11.5	90.5
3	0.0728	0.699	0.943	1 : 9.60 : 13.0	102.2
4	0.0728	0.699	0.889	1 : 9.60 : 12.2	76.8(2)
5	0.0791	1.45	0.912	1 :18.2 : 11.5	72.7(3)
6	0.0798	0.717	0.864	1 : 8.98 : 10.8	78.7(3)
7	0.1600	0.717	0.878	1 : 4.49 : 5.51	95.2(3)
8	0.0790	0.714	0.871	1 : 9.05 : 11.0	71.7(4)
9	0.1170	1.07	1.63	1 : 9.15 : 13.9	75.5
10	0.0792	0.833	1.25	1 :10.5 : 15.8	88.3

(1) 100% basis

(2) Gaseous products lost after infra-red sampling due to faulty valves. Value given represents only residual boron.

(3) Portion of product involved in infra-red sampling not included.

(4) Does not include volatilized boron compounds.

time, over the range investigated, produces no significant change in the amount of boron volatilized. In the earlier portion of this continuing investigation, a significantly longer heating time, 15 hours, had apparently increased the volatilized boron yield; however, this reaction had also included an excess of SO_3 over the stoichiometry indicated above.

Reactions 5, 6, and 7 were carried out in order to obtain gas samples for infra-red analysis. An absorption spectrum for the infra-red gas cell is shown in Figure 1. Notice should be taken that this absorption spectrum precludes the region 600 cm^{-1} to 1100 cm^{-1} from consideration in analyzing gas mixtures. In view of this circumstance, attention was focused only in the region 1100 cm^{-1} to 4000 cm^{-1}.

In order to provide spectra for comparison with those in the literature and spectra of samples obtained under the reaction conditions in this investigation, samples of known purity of BF_3, SF_6, SO_2F_2, and SO_3 - Figures II, III, IV, V, VI, and VII - were analyzed. With the exception of SO_3, the gas samples were obtained by flushing the respective gases, from lecture bottles, through the cell.

In order to obtain the SO_3 sample the gas cell was evacuated with a water aspirator, suitably arranged to prevent water vapor from entering, and connected to the SO_3 stock bottle. The SO_3 vapor was then drawn into the cell by opening the stopcock. Although other gases may be postulated as being in the product gas mixture, none other than the above were readily obtainable.

Spectra obtained on the gas product mixture for Experiments 5

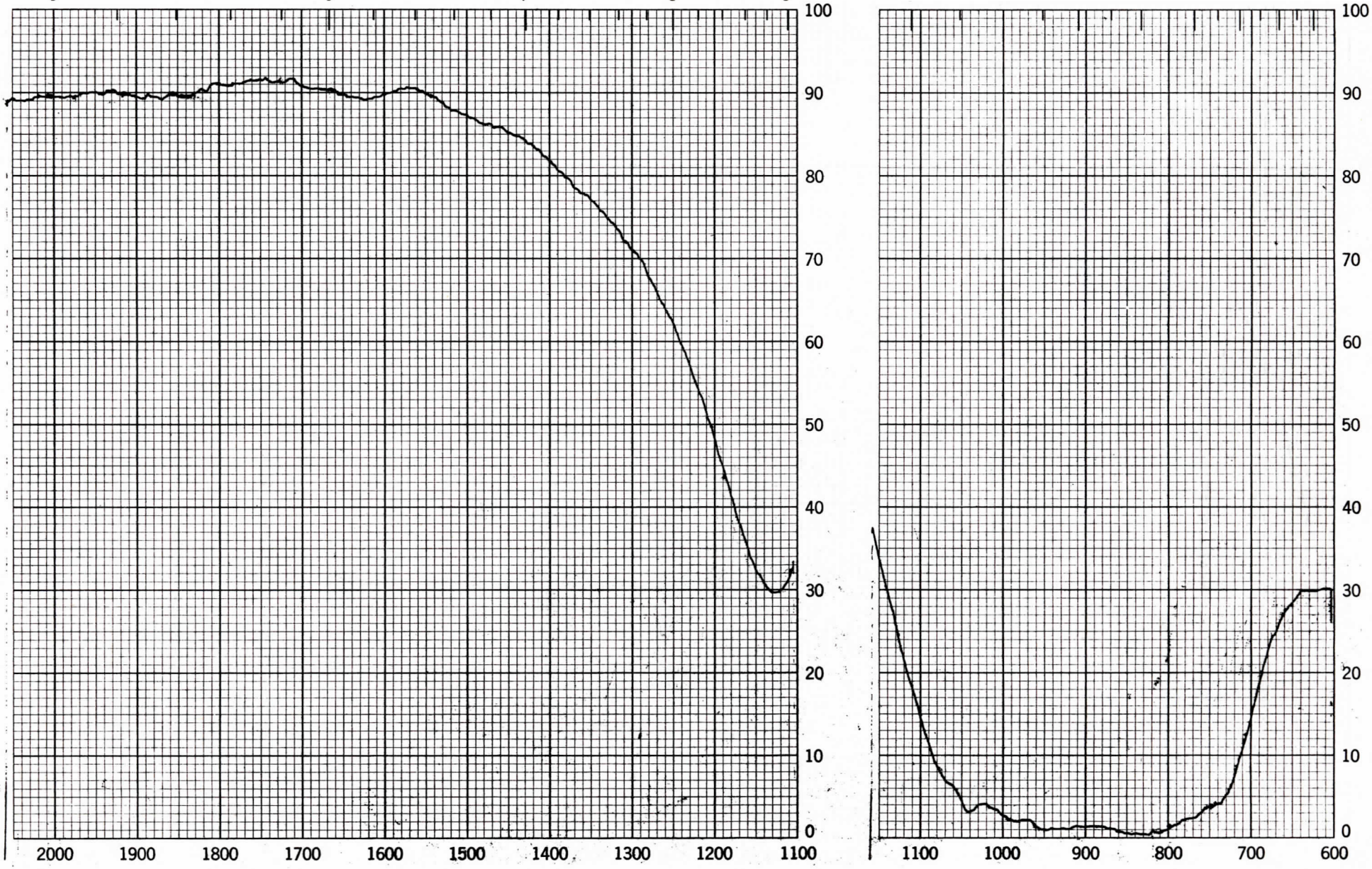

Figure I. Infra-Red Spectrum for Gas Cell Employing CaF_2 Windows

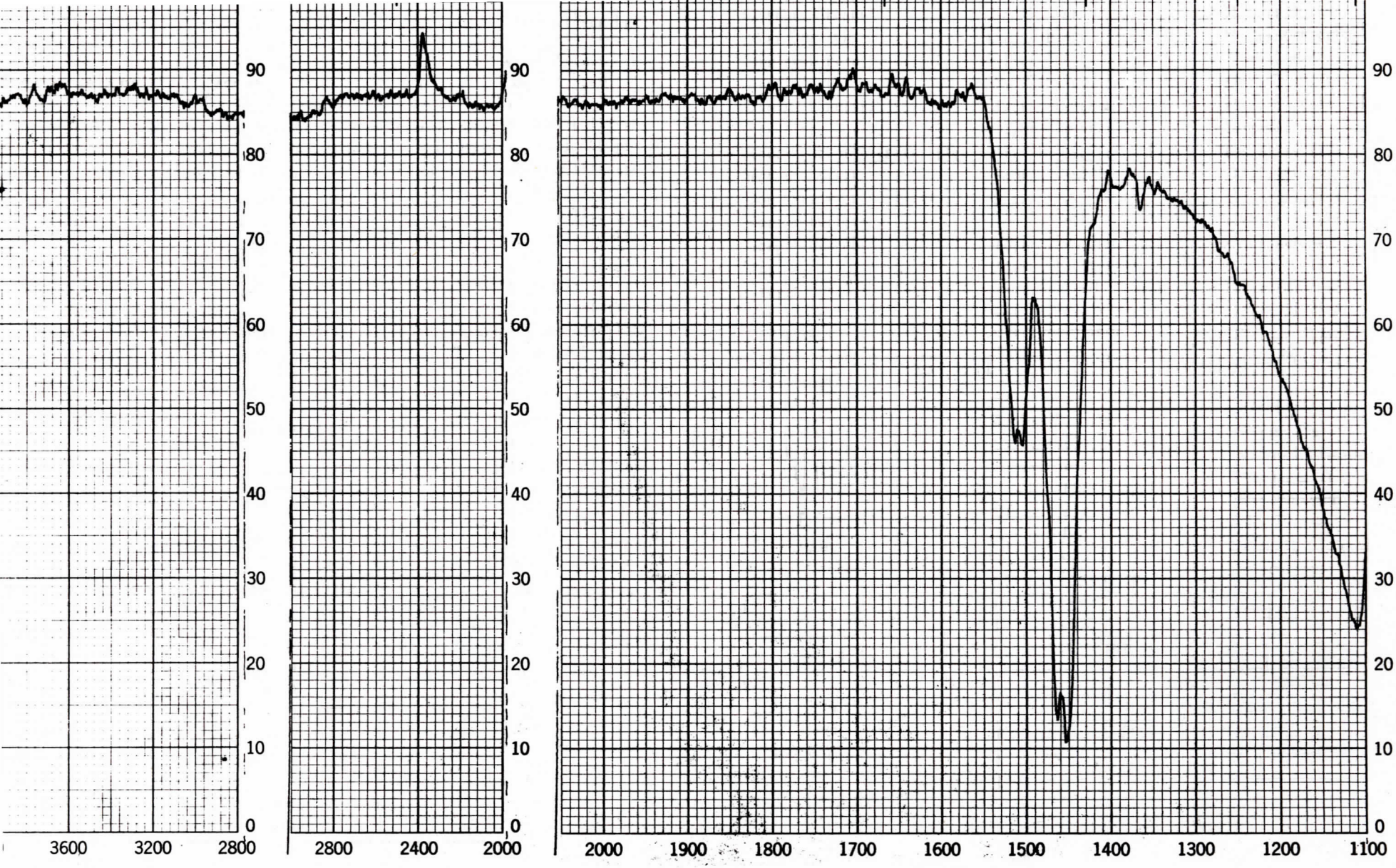

Figure II. Infra -Red Spectrum of BF_3 ($p < 1$ atm)

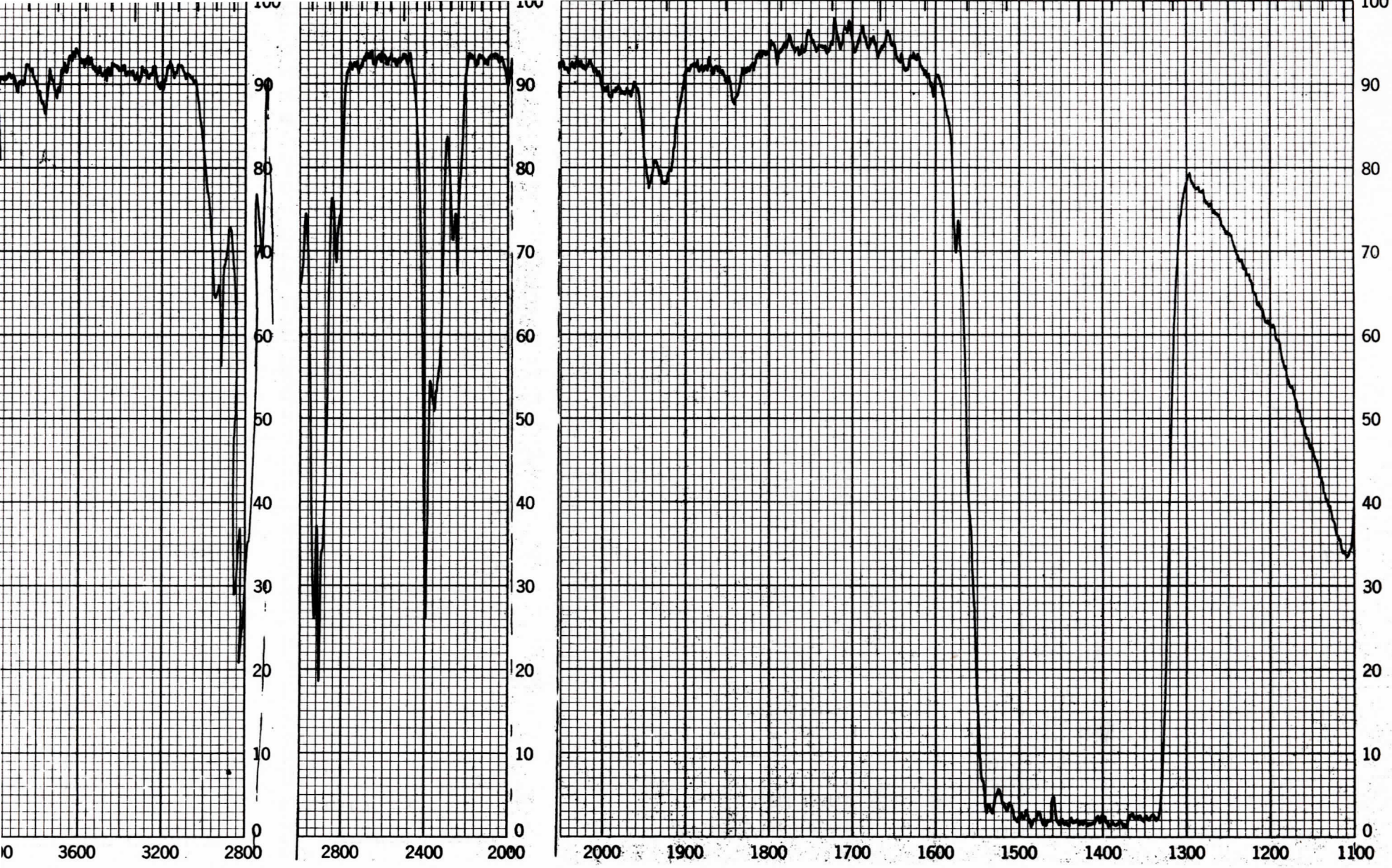

Figure III. Infra-Red Spectrum of BF_3 (p = 1 atm)

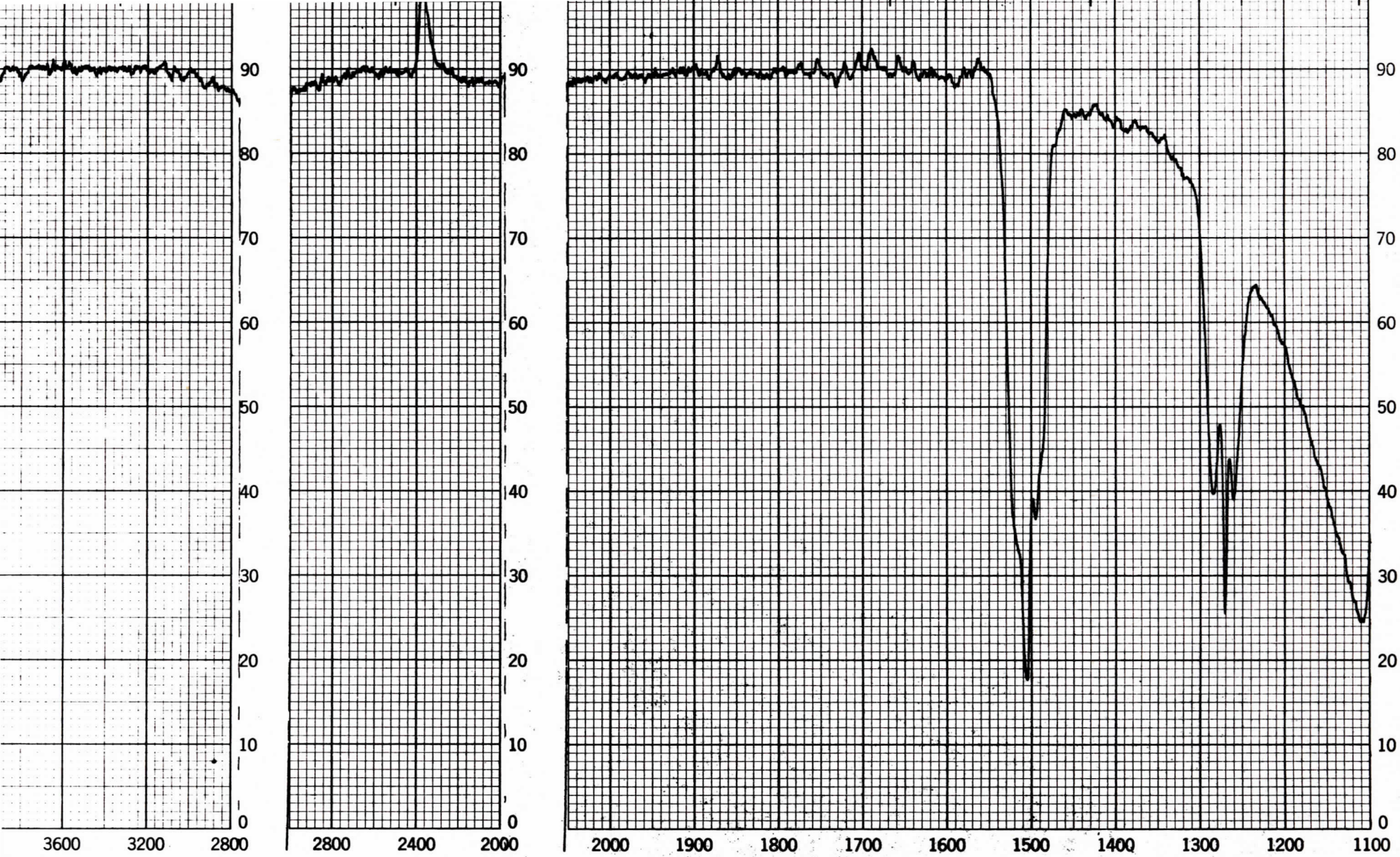

Figure IV. Infra-Red Spectrum of SO_2F_2 ($p < 1$ atm)

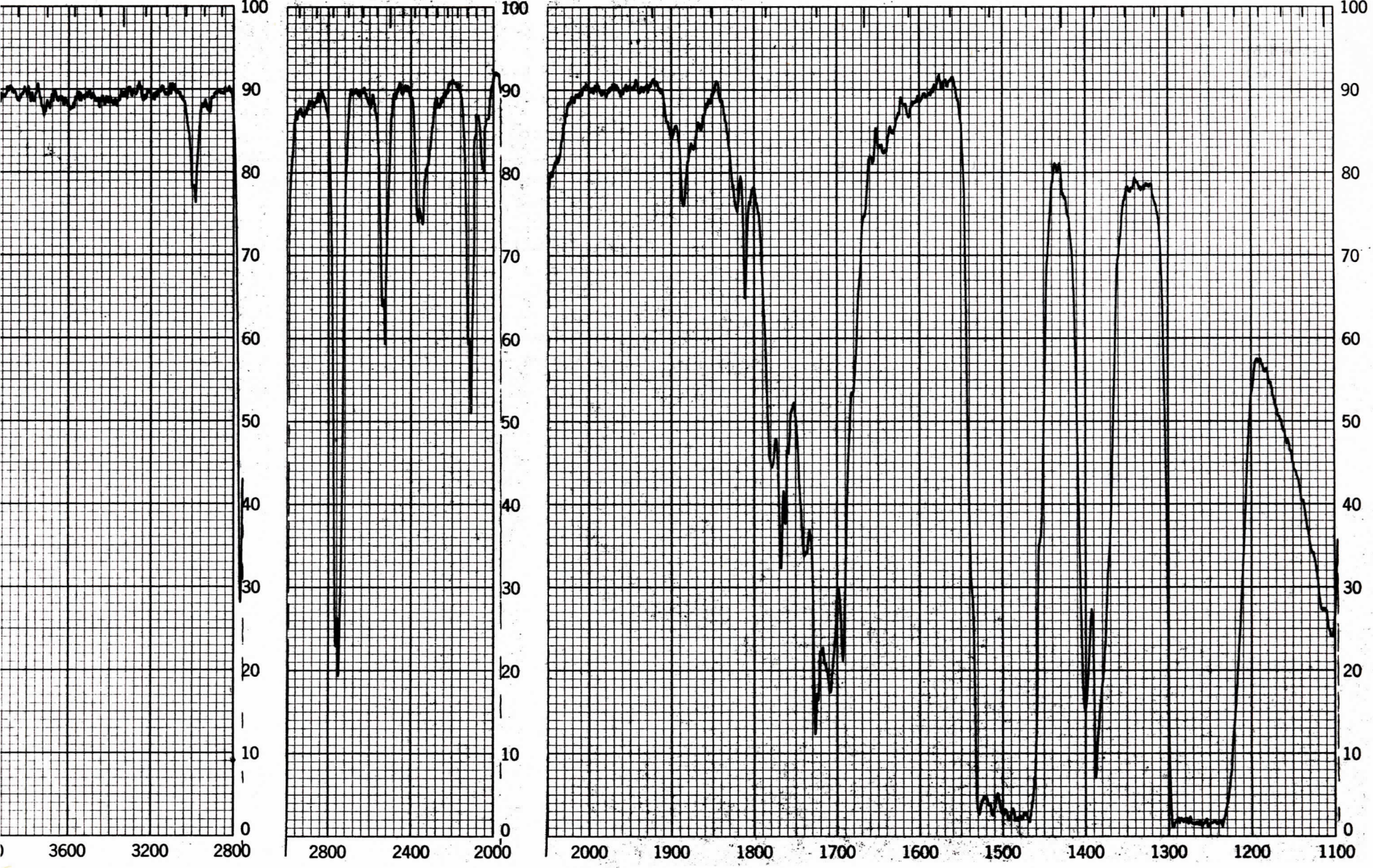

Figure V. Infra-Red Spectrum of SO_2F_2 (p = 1 atm)

Figure VI. Infra-Red Spectrum of SO_3 ($p < 1$ atm)

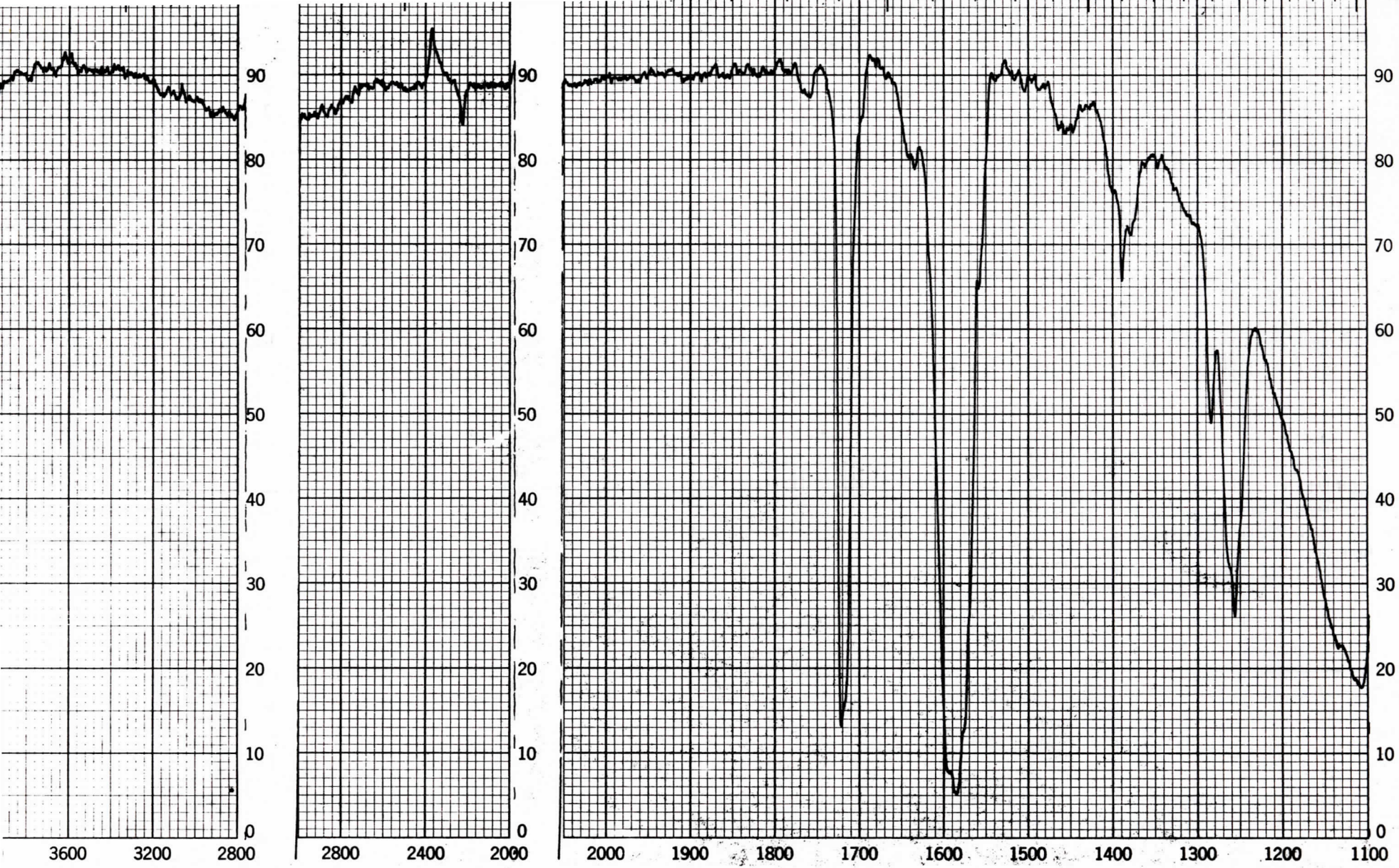

Figure VII. Infra-Red Spectrum of SF_6 ($p<1$ atm)

and 6 are shown in Figures VIII and IX. Figure VIII represents the product mixture, obtained by the procedure described in the Experimental section preceding and diluted with dry nitrogen to resolve the strongest peaks observed in the undiluted sample. Comparison of Figures II and VIII unequivocally indicates the presence of boron trifluoride in the product mixture as a major component.

In contrast, the spectrum shown in Figure IX, for the undiluted product mixture obtained from a typical reaction - Experiment 6 - shows that the product mixture is complex. Examination and comparison with the spectra for the pure sample gases, or with reported spectra, supports the earlier suspicion that SO_2F_2 was formed in the reaction. (In the first part of this investigation it was shown that SO_2F_2 was ineffective as a fluorinating agent.) The spectra also gave evidence for the presence of SiF_4; however, it cannot be ascertained whether the SiF_4 is a primary reaction product or if it resulted from the hydrolysis of BF_3 with trace moisture in the cell. Other possible components, e.g. thionyl fluoride, sulfur hexafluoride, sulfur trioxide, hydrogen fluoride, etc. were apparently not present in sufficient concentration to be detected under the operating conditions. It may be deduced from an examination of the data obtained from Experiments 5, 6, and 7 that a reaction occurs in the system which leads to the formation of sulfuryl fluoride and a concomitant decrease in the boron volatized. Conversely, the reaction does not appear to be favored when an excess of boron, as Colemanite, is present in the system.

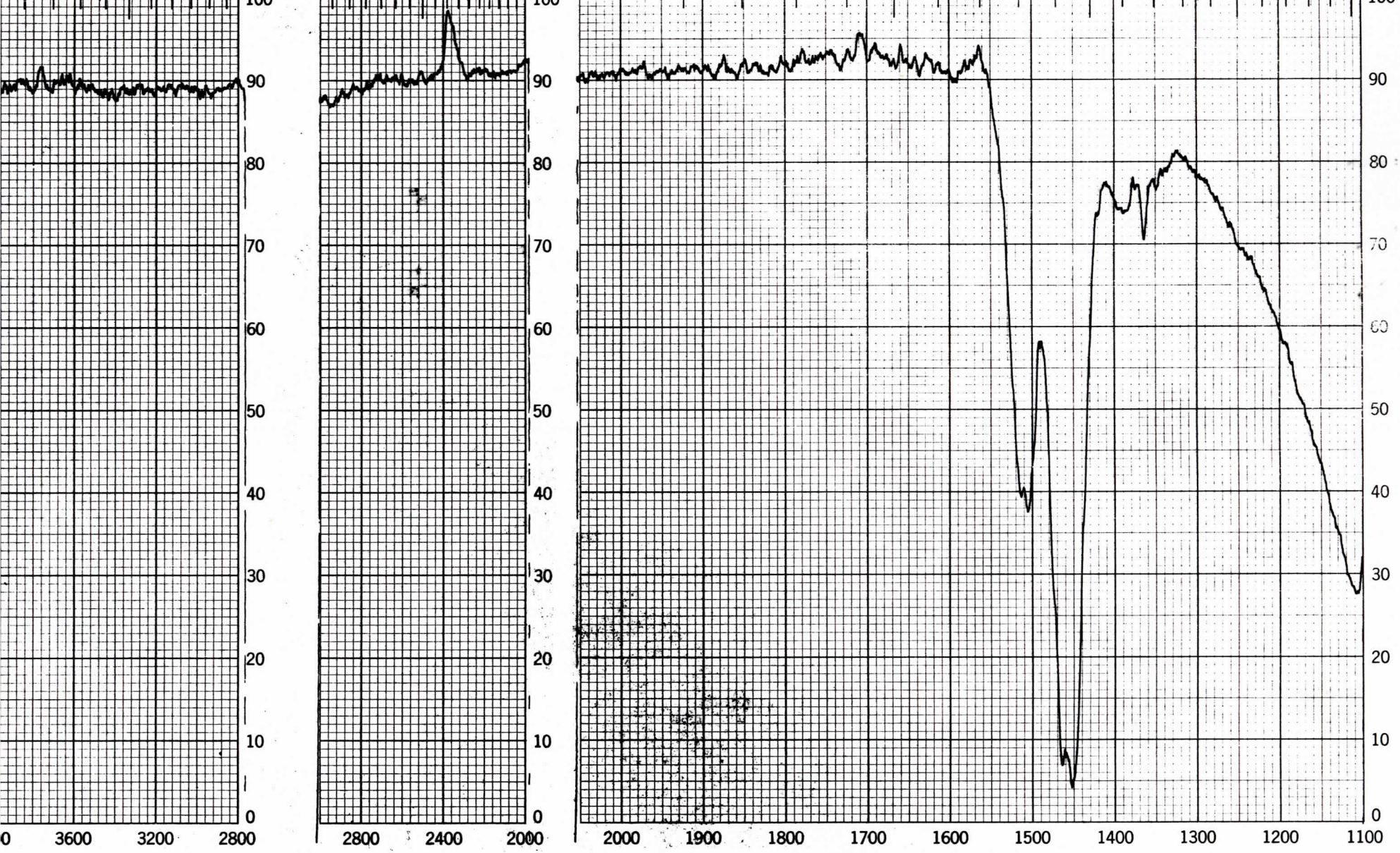

Figure VIII. Infra-Red Spectrum of Gaseous Reaction Product of Experiment 5 ($p < 1$ atm)

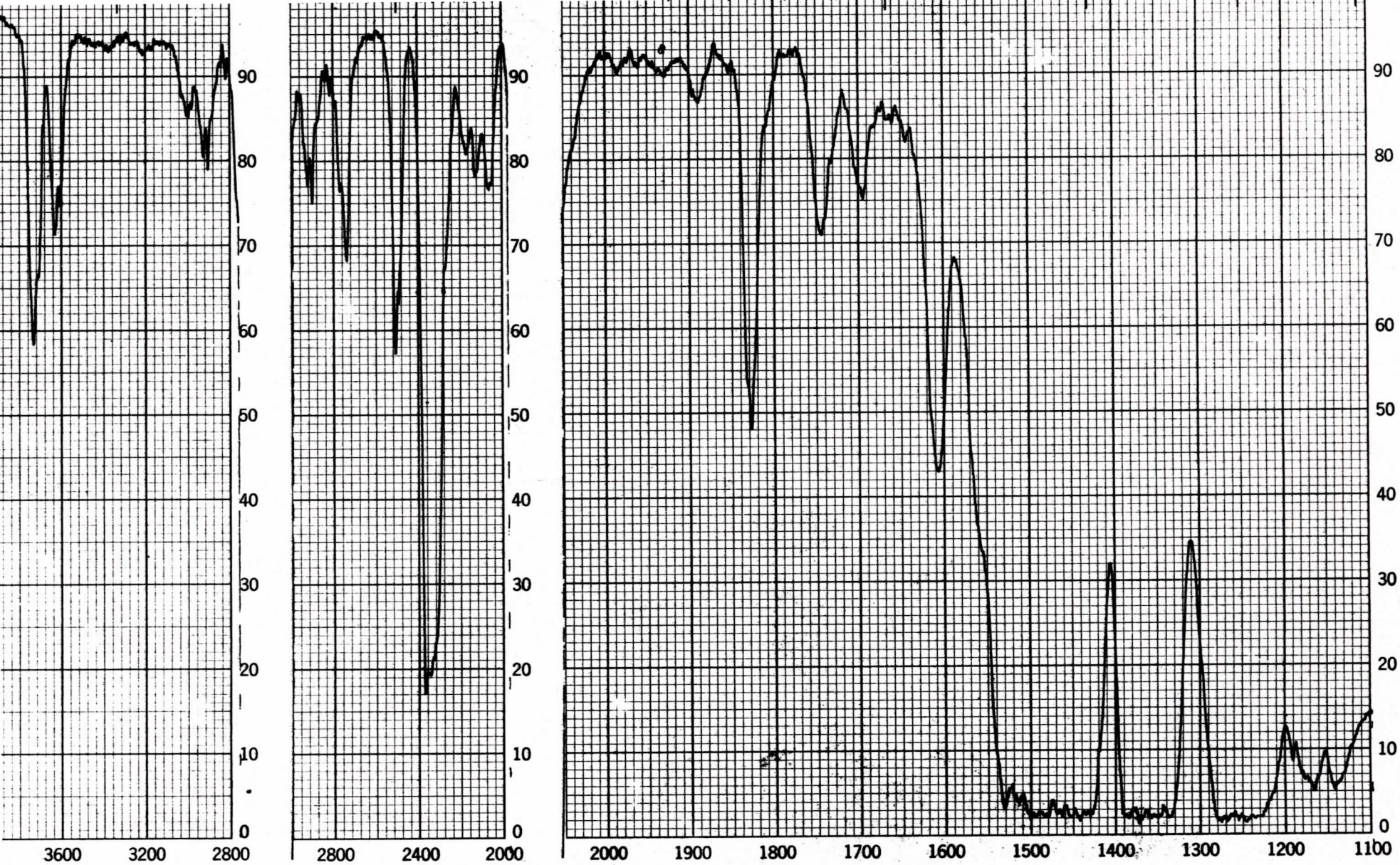

Figure IX. Infra-Red Spectrum of Gaseous Reaction Product of Experiment 6 (p = 1 atm)

In a further effort to explain the apparent presence of sulfuryl fluoride in the reaction product mixture, an experiment was carried out wherein calcium fluoride (fluorspar) and sulfur trioxide were reacted at a 1:1 molar ratio under the procedural conditions used throughout this investigation. The gaseous product recovered from this reaction was not identified by infra-red analysis as sulfuryl fluoride, nor as any of the other gases previously alluded to as possible products in these systems. In order to eliminate the possibility that impurities in the "fluorspar" calcium fluoride were responsible for this unanticipated result, a second similar experiment employing ACS reagent grade calcium fluoride was performed, for which the resultant spectrum was essentially the same. No reasonable explanation can be offered, at this time, for the product(s) obtained in this reaction. Since this gas is neither sulfur trioxide nor sulfuryl fluoride, insofar as the major component is concerned, it may be inferred that in the Colemanite reaction, wherein sulfuryl fluoride is identifiable in the product gas mixture, Colemanite is essential in some manner to the formation of sulfuryl fluoride. Further, it appears that the product from the CaF_2 - SO_3 reaction is also present in the Colemanite - CaF_2 - SO_3 reaction.

The remaining three reported reactions (Experiments 8, 9, and 10) involved the reaction between diethyl ether and the resultant reaction product gases in an effort to recover the boron trifluoride as the etherate adduct. In the first experiment - Experiment 8 - the ether employed was not obtained from sealed containers, and, upon recovery of the non-ether fraction, it was found that no $BF_3 \cdot Et_2O$ was obtained.

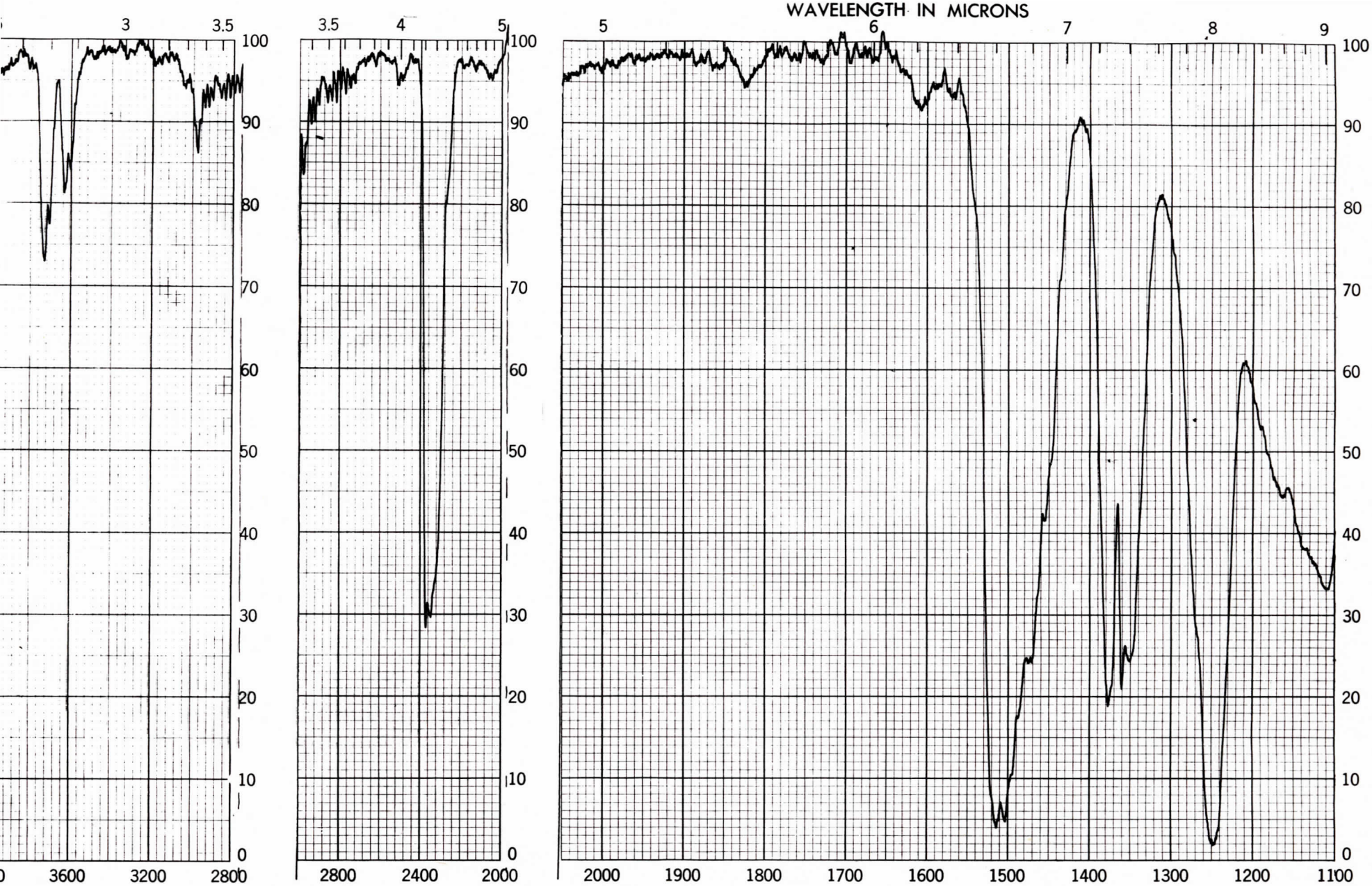

Figure X. Infra-Red Spectrum of Gaseous Reaction Product of CaF_2-SO_3 System

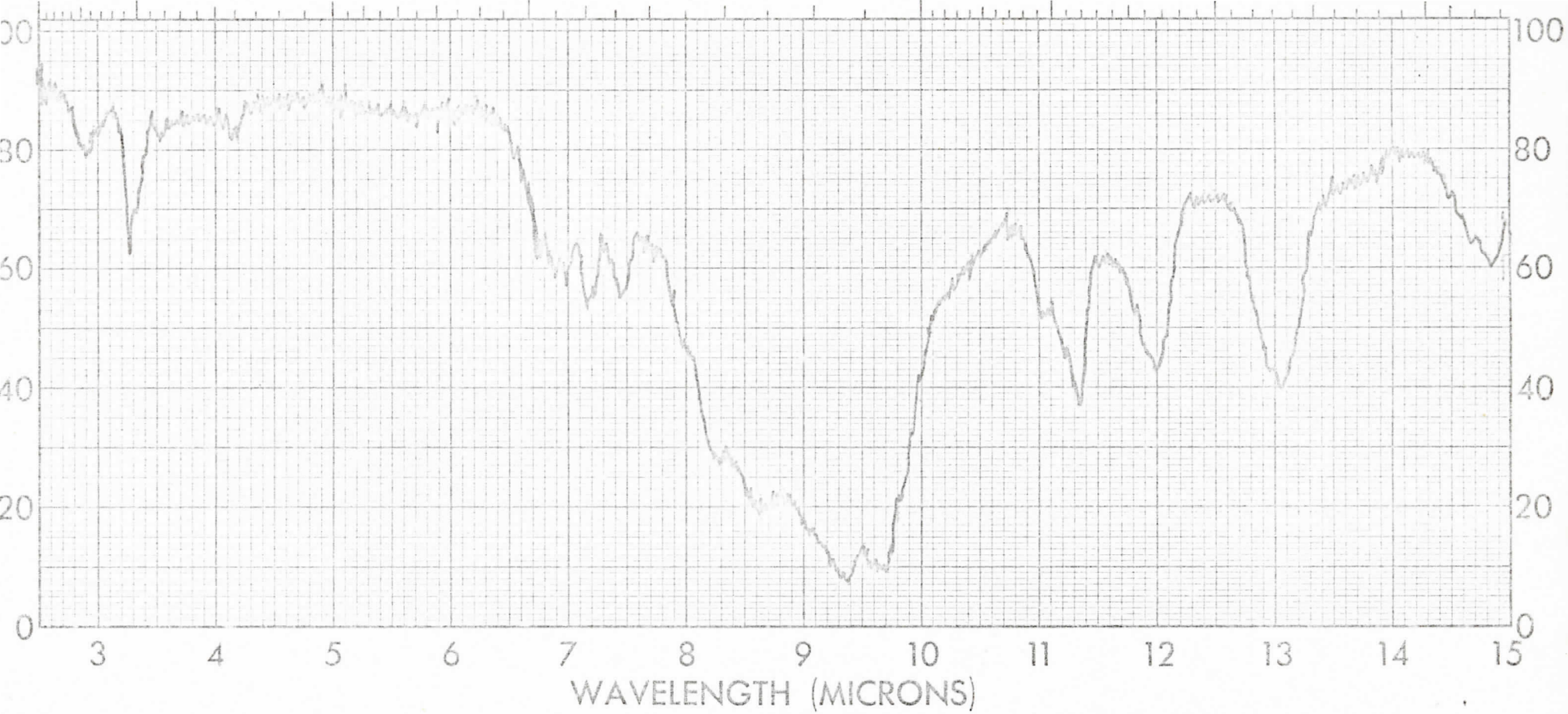

Figure XI. Infra-Red Spectrum of $BF_3 \cdot Et_2O$, Reaction 9

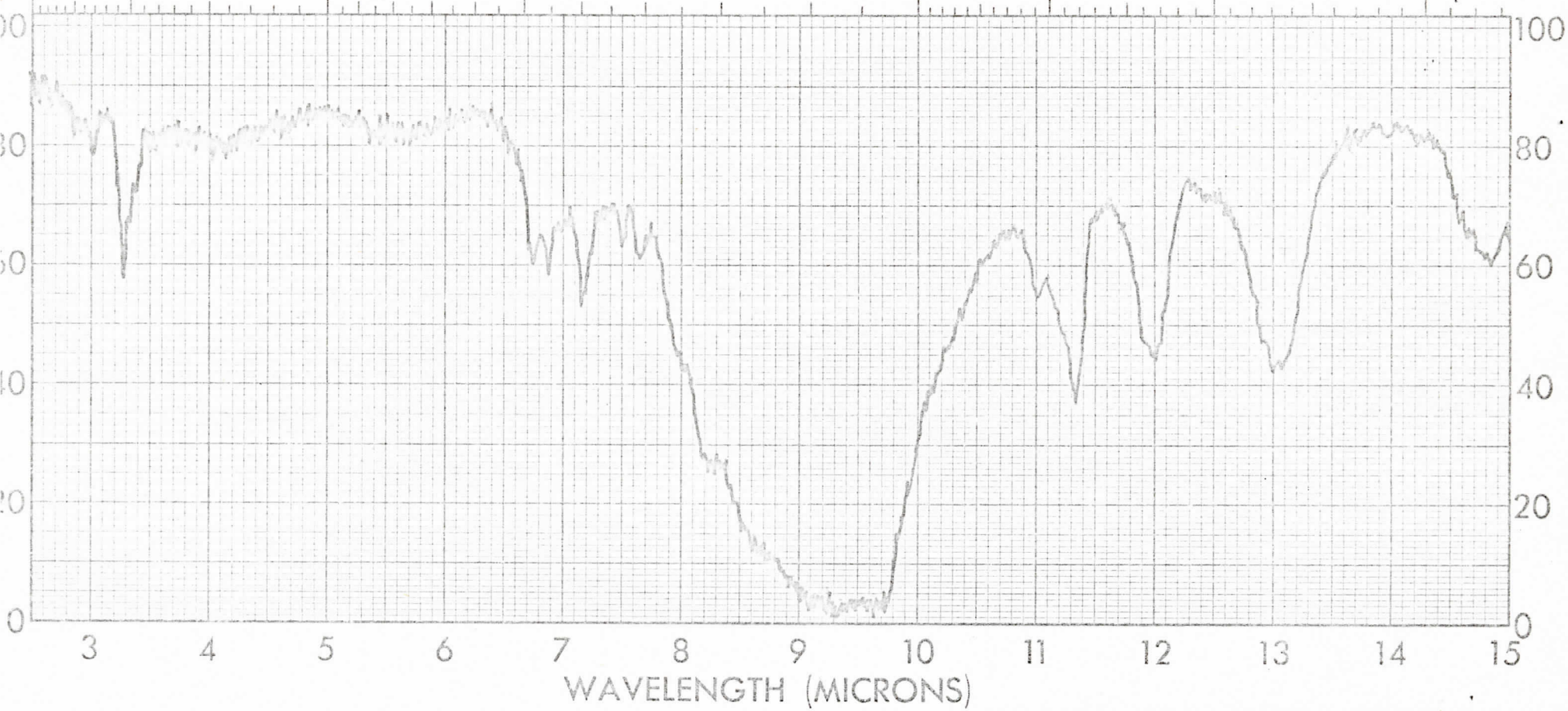

Figure XII. Infra -Red Spectrum of $BF_3 \cdot Et_2O$

Circumstances surrounding this unexpected turn of events led to the conclusion that hydrolysis had occurred, seemingly due to moisture in the ether. Accordingly, two similar experiments (9 and 10) were carried out from which $BF_3 \cdot Et_2O$ was obtained. Spectra for $BF_3 \cdot Et_2O$ obtained from the reaction and a sample prepared from pure BF_3 and ether are shown in Figures XI and XII respectively.

The boiling points of the standard etherate and the etherate recovered from reaction products were exactly similar, within the precision of the thermometer, viz. 122 °C. In addition, portions of the etherates obtained from the reactions were analyzed for boron content from which its presence was substantiated.

SUMMARY AND CONCLUSIONS

The foregoing discussion describes a number of reactions of the Colemanite - CaF_2 - SO_3 system related to further investigation into an economical method of preparing boron trifluoride from low cost starting materials. In this presentation primary effort was directed toward identification of the components of the gaseous reaction product, and to a convenient method of separating and recovering boron trifluoride from the mixture.

In addition to the identification of volatile boron compound, or compounds, by classical analytical methods, boron trifluoride, as well as other gaseous products, were identified in the gas mixture by infra-red analysis. Examination of the spectral data indicates that boron trifluoride is a major product of the reaction, even when reaction parameters are sufficiently changed so as to be less favorable for its production. When reaction conditions coincide with the proposed reaction stiochiometry, it appears that boron trifluoride is the major component of the product gas. With less certainty the idetification of sulfuryl fluoride and silicon tetrafluoride was made.

There is also in the product gas an as yet unidentified component, or components, which appear to be present under all reaction conditions and which is the principal product obtained from the reaction of calcium fluoride and sulfur trioxide, under the same reaction conditions. Although the conditions attendant upon sampling the gas might preclude the presence of sulfur trioxide, it is

reasonably certain that sulfur trioxide is not a major component of the gas phase after reaction.

Insofar as the second objective of the investigation is concerned, it was shown that the boron trifluoride can be recovered as the diethyl ether adduct, which can then be purified through fractional distillation to a desirable boron containing product. The recovery and positive identification, by infra-red analysis, of $BF_3 \cdot Et_2O$ although not constituting the primary evidence for the formation of BF_3 in the reaction, does further substantiate the evidence obtained by other means. In the formation of the etherate adduct, it is of prime importance that the ether be dry.

In the initial phase of the present work a preliminary investigation of the effect of heating time was conducted. The results obtained, insofar as the reaction periods were concerned, gave no new insight into the optimum conditions for maximum BF_3 yield. (In the first part of this two-part investigation, an increase in reaction time, 15 hours, coupled with an increase in the sulfur trioxide available for reaction, appeared to slightly increase the BF_3 yield.) Analysis of all the data available on the subject reaction leads to the conclusion that reaction times of the duration investigated do not significantly influence BF_3 yield; however, BF_3 yield is influenced by the amount of sulfur trioxide in the system.

As a result of the efforts made on the Colemanite - CaF_2-SO_3 system up to this time, a number of conditions relating to the characteristics of the reaction can be stated: (1) in all reactions the initial increase in pressure, attributed to the vaporization

of the SO_3, is followed, at the reaction temperature, by a sharp decrease in pressure; (2) sulfuryl fluoride, although detected in the reaction system, does not act as a fluorinating agent for Colemanite; (3) the reaction of CaF_2 with SO_3, in the absence of Colemanite, does not yield sulfuryl fluoride; (4) an unidentified gas which is the major product of the CaF_2-SO_3 reaction appears to be present in all the Colemanite-CaF_2-SO_3 reactions, and (5) variation in reaction time does not materially affect the BF_3 yield. From analysis of the foregoing statements of the known reaction characteristics several substantiative conclusions can be drawn.

The fluorine, introduced into the system as calcium fluoride, appears in the product gas mixture in several different forms, i.e. BF_3, SO_2F_2, and possibly others including the unidentified component(s) of the mixture. This conclusion leads to the suspicion that boron trifluoride production proceeds through the formation of an intermediate which acts as the fluorinating agent on boron in Colemanite. Also assuming that the intermediate is the same substance as that found in CaF_2-SO_3 reaction, use of this material as the fluorinating agent for Colemanite, would tend to delineate the course of the reaction.

The presence of sulfuryl fluoride in the reaction mixture, however, suggests that another reaction occurs which effectively decreases the amount of fluorine available for boron trifluoride production. On the basis of the information available the possibility that the same intermediate undergoes a reaction yielding the sulfuryl fluoride cannot be overlooked. In this regard it may be that a reaction time corresponding to the time of occurrence of the sharp

pressure decrease would be more inducive to increased boron trifluoride yield than longer heating times. Concomitantly a more intensive study of the sulfuryl fluoride production, with regard to reaction time, would appear to be advisable particularly since it has been shown that sulfuryl fluoride does not act as the fluorinating agent for Colemanite in this system.

Thus far study of the Colemanite reaction system has centered on reactions involving the boron, and to a lesser degree, sulfur trioxide. It would appear that a further study of the reaction leading to the maximization of boron trifluoride yield is dependent upon a knowledge of the part that fluorine plays in the obviously complex system.

APPENDIX: VALVE CARE AND MAINTENANCE

Because of the corrosive nature of the reactants and products of the Colemanite -CaF_2-SO_3 system the valves on the reactor, particularly the exit valve, are subject to faulty behavior. Although this behavior cannot be predicted it can be minimized by proper valve care as follows:

(1) Careful disassembly and cleaning followed by inspection to insure the absence of foreign material on the valve seat and needle,

(2) At the slightest indication of corrosion on the needle, polishing of the tapered portion with extra fine steel wool,

(3) In evacuating the reactor, prior to admission of the SO_3, the valve must be opened very slowly.

In those cases where a valve shows pitting on the needle surface only, the usable life of the valve can be prolonged by careful machining of the tapered surface. Experience has shown that where pitting has occurred involving the seat that the valve could not be reliably repaired.

LIST OF REFERENCES

1. Bailey, C. R., J. B. Hale, and J. W. Thompson, Proc. Roy. Soc., 161, 107 (1937).

2. Bailey, C. R., J. B. Hale, and J. W. Thompson, J. Chem. Phys., 5, 274 (1937).

3. Furman, N. H. (ed.), "Scott's Standard Methods of Chemical Analysis," Vol. 1, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1939, pp. 174-175.

4. Gage, D. M., and E. F. Barker, J. Chem. Phys., 7, 455 (1939).

5. Gaunt, J., Trans. Faraday Soc., 1953, 49, 1122.

6. Jones, E. A., J. S. Kirby-Smith, P. J. H. Woltz, and A. H. Nielsen, J. Chem. Phys., 19, 242 (1950).

7. Kuipers, G. A., D. F. Smith, and A. H. Nielsen, J. Chem. Phys., 25,275 (1956).

8. Laubengayer, A. W., and G. R. Finlay, J. Am. Chem. Soc., 55, 2858 (1933).

9. O'Loane, J. K. and M. K. Wilson, J. Chem. Phys., 23, 1313 (1954).

10. Pace, E. L., and L. Pierce, J. Chem. Phys., 23, 1248 (1954).

11. Perkins, W. D., and M. K. Wilson, J. Chem. Phys., 20, 1791 (1952).

12. Rhyne, Thomas Crowell, "An Investigation of a Method of Preparation of Boron Trifluoride From Colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)." Unpublished Master's dissertation, Department of Chemistry, Appalachian State Teachers College, 1967.