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ASD-TDR-62-1025
VOLUME III of V

This document consists of _____ pages
No. 2 of _____ copies, Serial A

(Unclassified Title)

FINAL REPORT FOR HIGH ENERGY FUELS PROJECT
VOLUME III. PROCESS DEVELOPMENT FOR DIBORANE PRODUCTION

TECHNICAL DOCUMENTARY REPORT NR. ASD-TDR-62-1025. VOLUME III

JUNE 1962

CHEMICAL ENGINEERING BRANCH
MANUFACTURING TECHNOLOGY LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

ASD PROJECT NR. 7-5586

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Prepared Under Contract AF 33(600)-3574A

AFN, Inc.
LOS ANGELES 5, CALIFORNIA
Author: Dr. T. W. Clapper

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June 1962

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FOREWORD

Volume Three of this Final Technical Documentary Report covers all work performed for the process development for diborane production under Contract AF 33(600)-35745 from September 1957 to March 1962. The manuscript was released by the author on 15 June 1962 for publication as an ASD Technical Documentary Report.

This contract with AFN, Inc. comprised of American Potash & Chemical Corporation, FMC Corporation, and National Distillers and Chemical Corporation, with main offices located in Los Angeles, California, was initiated under Manufacturing Methods Project 7-558b, "High Energy Fuels Project." It was accomplished under the technical direction of Mr. Charles Tanis, Chemical Engineering Branch, (ASRCTC), Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Dr. T. W. Clapper of American Potash & Chemical Corporation was Project Manager. Others who cooperated in the supervision of this project and in the preparation of the report were: R. C. Rhees and C. B. Armstrong of American Potash & Chemical Corporation, J. A. Bergantz of FMC Corporation, and D. Horvitz of National Distillers and Chemical Corporation.

This project has been carried out as a part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. This program encompasses the following technical areas:

Rolled Sheet, Forgings, Extrusions, Castings, Fiber and Powder Metallurgy
Component Fabrication, Joining, Forming, Materials Removal
Fuels, Lubricants, Ceramics, Graphites, Non-Metallic Structural Materials
Solid State Devices, Passive Devices, Thermionic Devices

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

Volumes I, III, IV and V of this report are classified CONFIDENTIAL because they disclose new, novel and unique methods of producing and processing certain boron hydrides.

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FINAL REPORT FOR HIGH ENERGY FUELS PROJECT
PROCESS DEVELOPMENT FOR DIBORANE PRODUCTION

A direct and economical process for the manufacture of high purity diborane is provided by the silver-catalyzed hydrogenation of boron trichloride and the disproportionation of the dichloroborane formed. Pilot plant operating data and experience were accumulated for the design of a large scale plant.

Initially, two variations of the sodium borohydride-boron trichloride reaction successfully and routinely produced diborane in satisfactory yield and purity in a total of 109 prepilot plant runs. Both methods first converted sodium hydride, made as a mineral oil slurry by the hydrogenation of metallic sodium, to sodium borohydride; however, one method avoided the isolation of NaBH_4 and utilized an in situ reaction with boron trichloride to produce diborane. This method employed mineral oil as the primary vehicle, thereby largely eliminating the costly solvents necessary to the earlier process. The by-product salt was also more readily filtered. An average diborane purity of 89 per cent and an average yield of 74 per cent, based on boron trichloride consumed, were achieved in twenty consecutive prepilot plant runs.

A fifty pound per day pilot plant was designed, built and operated, employing a unique diborane process developed through laboratory and prepilot plant investigations. This process does not require an active metal. Instead, boron trichloride is directly reduced with hydrogen to form dichloroborane in a silver-lined catalytic reactor operating at 1275°F. and 250 psig. The dichloroborane is separated, concentrated, and disproportionated to form diborane in conventional absorption and distillation equipment of ordinary materials of construction. Important features of the process include a quick-quench of the reactor effluent to "freeze" the favorable equilibrium existing at the higher temperature, and the multiple utilization of boron trichloride as an absorbent and solvent as well as reactant. Side reactions are minor. Pilot plant operations demonstrated the production of diborane and by-product anhydrous hydrogen chloride in 99 per cent purity and 96 per cent yields, and provided the necessary data and experience for a larger scale plant design.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:


JACK R. MARSH
Assistant Chief
Manufacturing Technology Laboratory
Directorate of Materials & Processes

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INTRODUCTION

The first practical methods for the manufacture of diborane involved the use of one or more active metals. Sodium was selected by AFN, Inc. for use in its original diborane process. Proprietary sodium technology possessed by National Distillers and Chemical Corporation, one of the AFN partners, would be important in the design and operation of a large scale boron hydrides plant requiring efficient recovery of the active metal.

Thus the original contract [AF 33(600)-35745] with the Air Force called for (in part) AFN's "study and evaluation of the boron trichloride-sodium borohydride reaction for producing diborane." Section 1 of this volume presents the information gained in the period September 1957 - November 1959 through prepilot plant investigations and related laboratory support activities devoted to the fulfillment of this objective.

In 1958, utilizing private funds, AFN, Inc. demonstrated in the laboratory that the hydrogenation of boron trichloride to form dichloroborane, followed by the latter's disproportionation, was a practical route to diborane. The economic advantage of such a direct process which avoids the use of an active metal was obvious. On this basis, a contract extension was granted to AFN for the purpose of further evaluating and developing the process. This work culminated in the design and operation of a pilot plant at Henderson, Nevada and provided the basis for the design of a large scale plant as presented in Volume I of this report. Section 2 of this Volume III reports the entire development program pertaining to this new process for diborane manufacture.

This total report consists of five (5) volumes, viz.:

- I. (U) Preliminary Design for a Large Scale Borane Plant
- II. (U) Theory of Diborane Pyrolysis
- III. (U) Process Development for Diborane Production
- IV. (U) Process Development for Diborane Pyrolysis
- V. (U) Process Development for Decaborane Alkylation

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SECTION ONE - SODIUM ROUTE

BACKGROUND INFORMATION

The potential importance of the boron hydrides as high energy fuels prompted AFN, Inc. to construct at its own expense a pilot plant for producing decaborane. This unit, operated for almost two years beginning in early 1957, provided a source of practical knowledge regarding diborane generation by the reaction of sodium borohydride with boron trichloride:



Ansul Ether 181 (dimethyl ether of tetraethylene glycol) was used as the sodium borohydride solvent and reaction medium.

In addition, a method for producing sodium borohydride was developed in the laboratories of American Potash & Chemical Corporation, again with private funds. First, two processes were investigated for the manufacture of sodium hydride based on the direct hydrogenation of sodium, according to the reaction:



One produced a dry, granular product; the other yielded a slurry in mineral oil. Yields and product purity of approximately 99 per cent were achieved by both methods.

Second, a sodium borohydride process not dependent on the usual extractive techniques was developed. In this process, sodium hydride was reacted with methyl borate in a solution of tetrahydrofuran and excess methyl borate. The insoluble borohydride was filtered from the medium, sodium methylate remaining in solution. The medium was then neutralized with a boron halide to produce the insoluble sodium halide and to regenerate methyl borate, bringing the solution back to its original composition.

The first step is represented as follows:



where B(OR)_3 is a borate ester, methyl borate in this case.

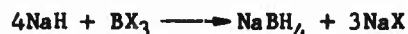
The second step proceeds according to the reaction:



where X is a halogen.

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The over-all reaction is:



Both boron trichloride and boron trifluoride proved satisfactory in the regeneration step although each offered a particular advantage. The former reagent is the more economical, but the latter produced a more readily filtered salt in the neutralization step. Both results are due to the partial formation of sodium fluoborate, rather than the simple sodium fluoride salt, when boron trifluoride is used.

After the laboratory scale work indicated the feasibility of this process, a bench-scale pilot plant was built to gather more definitive data for design of the prepilot plant. A series of eighteen runs, utilizing a mineral oil slurry of sodium hydride as feed material, demonstrated that sodium borohydride of 90 to 99 per cent purity and in 80 to 90 per cent yield (based on sodium hydride) could be obtained. A design basis of 95 per cent purity and 85 per cent yield was recommended.

These combined activities produced the needed information for the original design of the five pound per day HEF prepilot plant with very little additional Air Force sponsored laboratory investigation being required.

As the prepilot plant program developed, however, an important process improvement was originated. Laboratory and bench-scale activities preceded the incorporation of this process modification in the prepilot plant and are reported in this section.

SUMMARY

A prepilot plant, sized for the production of five pounds per day of finished product, HEF-3, was designed and constructed on the basis of data gathered in company-sponsored development programs. Twenty diborane generation runs were completed in this unit. Diborane purity averaged 85 per cent and the yield, based on sodium borohydride consumed, averaged 87 per cent, substantially above the 67 per cent used for design purposes. Equipment performance was generally satisfactory.

Some difficulty was experienced in the preparation of crystalline sodium borohydride; sodium hydride of the highest quality was found to be essential to the production of satisfactory sodium borohydride. Purity of the sodium borohydride reached 98.6 per cent and yields, based on sodium charged to the sodium hydride reactors, achieved the design figure of 83.4 per cent. Salt produced in boron trichloride neutralized

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batches was very difficult to remove by filtration, but a satisfactory aqueous separation method was developed. Salt was readily filtered from batches neutralized with boron trifluoride.

A greatly simplified variation of the original process was developed in the laboratory. This method eliminated the methyl borate-tetrahydrofuran solvent system from the sodium borohydride process as well as the need for isolation of crystalline sodium borohydride. Instead, boron trichloride was reacted with sodium hydride in a medium of 90 per cent mineral oil-10 per cent Ansul Ether 141 to form a slurry containing both sodium borohydride and salt. Further addition of boron trichloride to the slurry resulted in diborane generation.

The prepilot plant was modified to accommodate this development, and an additional 89 diborane generation runs were completed with the operation becoming routine. Somewhat increased diborane purity and yields were obtained. Filtering characteristics of the by-product sodium chloride were greatly improved.

PREPILOT PLANT DESIGN

I. Sodium Borohydride Production

The mineral oil process for sodium borohydride production was adopted for the prepilot plant for the following reasons:

1. Dry sodium hydride is dusty, pyrophoric and presents a serious fire hazard either alone or in a mixture with solvents. On the other hand, hydride particles protected by a film of oil in a mineral oil-hydride slurry are relatively safe to handle.
2. Hydride slurries can be handled as pumpable liquids, a definite processing advantage compared to handling a dry powder in an inert atmosphere.
3. The dry sodium hydride process was very difficult to control and required the attention of a highly skilled operator. A large scale plant would require extensive and intricate instrumentation. The mineral oil-sodium process had been used commercially and did not have these special requirements.
4. Lower temperatures were used in the mineral oil process, 200°C versus 350°C for the dry process.

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5. Lower hydrogen pressures were used in the mineral oil process, 10 psig versus 50 psig for the dry process.
6. Agitator shafts were easier to seal against hydrogen leaks in the mineral oil process since oil could be used as a sealant.

The engineering drawings in Appendix A include information pertinent to this part of the process. The general arrangement of equipment, along with heat and material balances, are presented. Step I relates to sodium hydride production, and Step II, to sodium borohydride. Prepilot plant equipment is pictured in Figures 1, 2 and 3.

Sodium was fed by gravity from a solid-pak drum on a stand above the sodium hydride reactor. Electrical band heaters melted the sodium in the steel drum. Hydrogen was supplied from a bank of 230 cubic foot cylinders located outside of the immediate processing area, while the mineral oil flowed by gravity into the sodium hydride reactor from a 100-gallon storage vessel (T-1), also located outside the area.

A steel centrifugal pump (P-1) was specified for the transfer of the sodium hydride-in-oil dispersion into the sodium borohydride reactor.

A sodium hydride reactor (R-1) of the following specifications was selected: 125 gallons, carbon steel, jacketed, internally baffled vessel, rated for internal pressure of 150 psig at 300°C; Premier 6 inch diameter Type No. 3400 dispersator, 10 h.p. 2400 rpm, agitator drive, Aroclor (high temperature heat transfer medium) to be pumped through the jacket to heat or cool the reactor as required.

Design specifications called for operation of this step basically as a batch process to obtain data and information so that a continuous dispersator and hydrogenator could be designed for a large scale operation.

A 500-gallon Pfaudler stainless steel jacketed reactor (R-2) was installed as the principal reactor in the sodium borohydride step of the process. A mineral oil sealant was used for the agitator double mechanical seal. Refluxing and distillation was carried out with a 35 square foot, stainless steel condenser (E-1) mounted above R-2.

To minimize the fire hazard, process liquors were stored in vessels located outside of the operating building. Two 500-gallon stainless steel holding tanks (T-3 and T-4) were installed outside, but were still only ten feet from R-2. A 75-gallon stainless steel receiver (T-2) was also located outside for storage of tetrahydrofuran. This vessel, mounted above grade, received new and distilled (to remove the stabilizer-hydroquinone) tetrahydrofuran in 55-gallon batches, as distillate from

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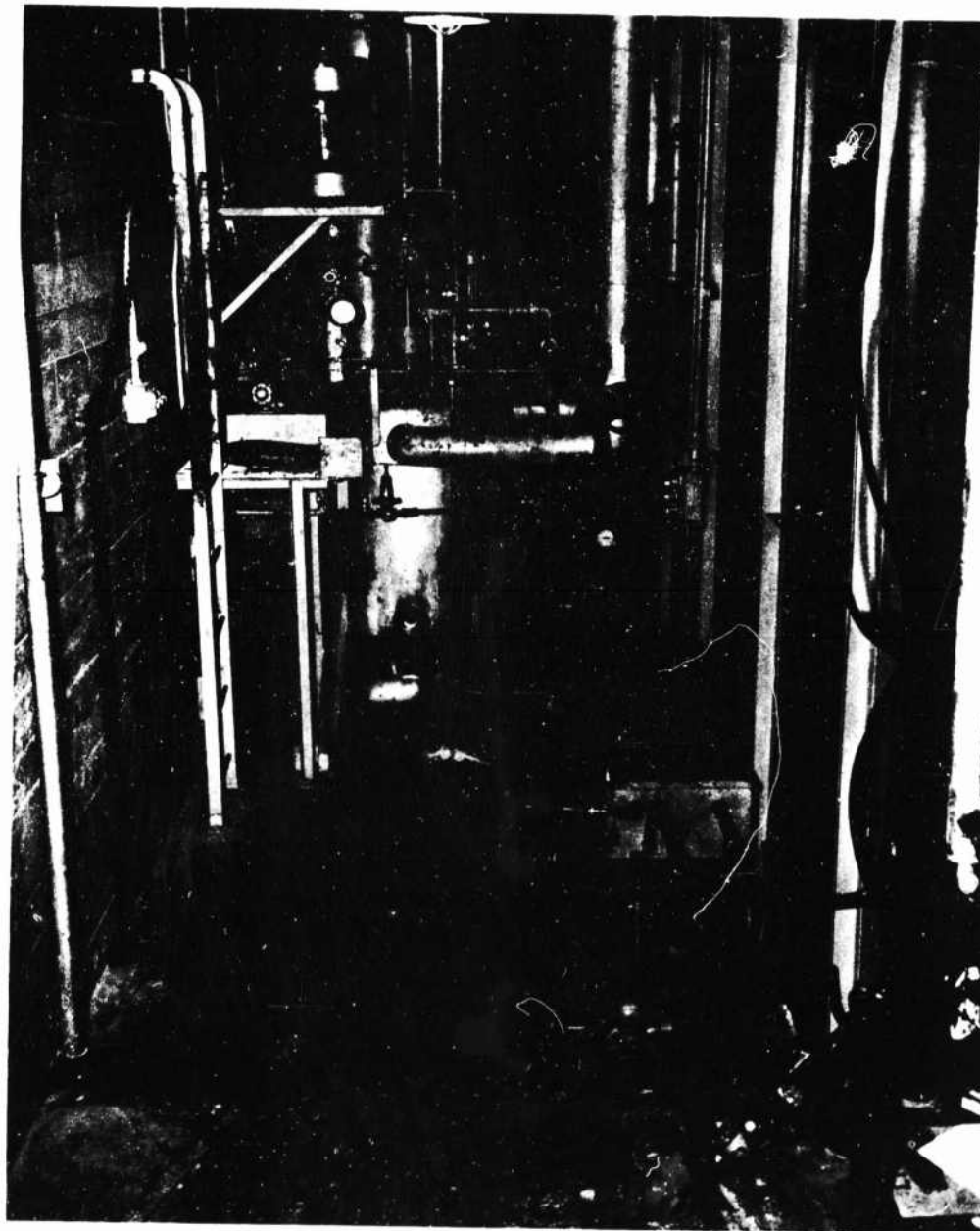


FIGURE 1. AFN PREPILOT PLANT
SODIUM HYDRIDE REACTOR

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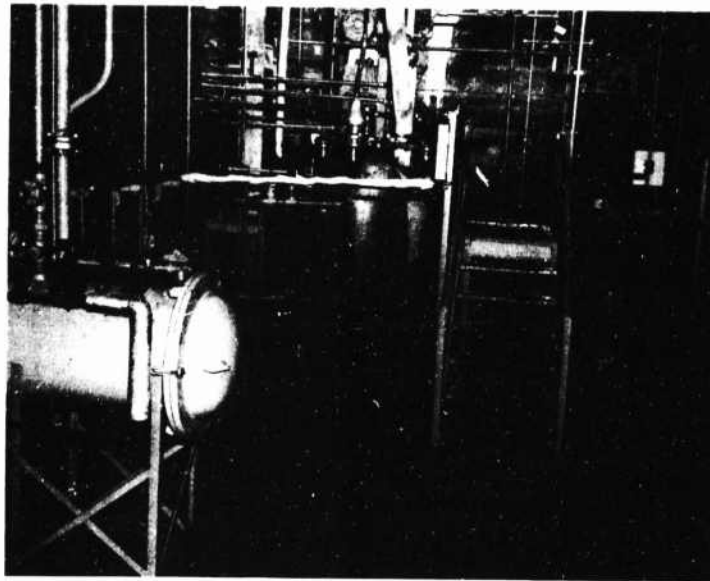


FIGURE 2. AFN PREPILOT PLANT
SODIUM BOROHYDRIDE REACTOR AND VACUUM DRYER

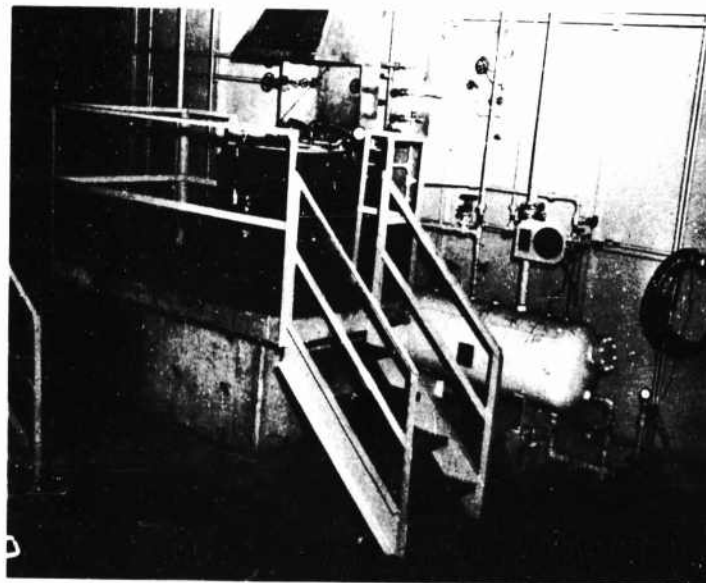


FIGURE 3. AFN PREPILOT PLANT
SODIUM BOROHYDRIDE CENTRIFUGE

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R-2. Make-up quantities required in the process liquors were fed into R-2 by gravity.

The flow of sodium hydride into R-2 was checked by a Bowser "flapper-type" flow meter. A 20-gallon per minute stainless steel Chempump permitted transfer of process liquors from R-2, and solvents from T-3 and T-4.

A perforate basket centrifuge designed for vacuum or pressure operation was installed for recovery of the sodium borohydride and the sodium halide from the process liquors. This unit, K-3, was a Tolhurst batch "center-slung" centrifuge, 20 inch diameter with a 2 h.p., two-speed drive. Filtrate from the centrifuge was collected in a 100-gallon, horizontal, stainless steel receiver (T-22) and transferred by means of a Chempump (P-26).

Sodium borohydride was vacuum dried in a steam heated, carbon steel tray dryer (D-1) in stainless steel trays. Plant vacuum (25" Hg.) from a Nash Hytor vacuum pump was connected to D-1.

Units added during the course of operations were (1) an open, 500-gallon tank for water washing of recycle oil, and (2) a Hilco Oil Reclaimer for final purification of the oil.

II. Diborane Production

Sodium borohydride, as produced in Step II, was dissolved in recycle Ansul Ether 181 (DTG) in a 100-gallon stainless steel vessel (T-5). A double interlock feed hopper permitted the feeding of sodium borohydride powder into the processing system without the introduction of air. This unit and other items of equipment in the diborane generating area are shown in Figure 4. They were preassembled on skids prior to being integrated into the prepilot plant. The control panel for this part of the operation is shown in Figure 5. Again, drawings in Appendix A present heat and material balances, and show the general arrangement of equipment. A propeller agitator with a double mechanical seal and DTG sealant provided agitation required to dissolve the borohydride solids. A stainless steel Chempump (P-5) transferred the feed solution to the diborane absorption column (C-2) and subsequently to the feed tank (T-6).

T-6, a 100-gallon stainless steel vessel, served as the feed tank for the borohydride solution pumped to the diborane reactor (R-3). A stainless steel, Lapp Pulsafeeder diaphragm pump (P-4) served to pump the feed liquor at a constant, controlled and metered rate.

The diborane generator (R-3) was a carbon steel, water-jacketed screw conveyor mounted directly above T-6 and the spent liquor tank (T-7). In

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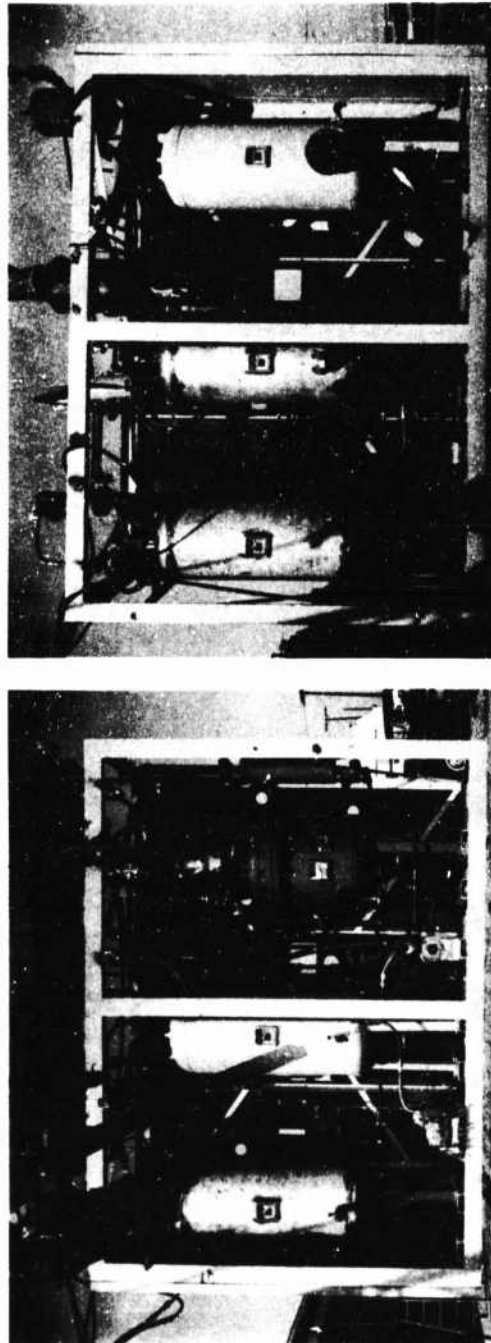


FIGURE 4. AFN PREPILOT PLANT
PROCESSING UNIT

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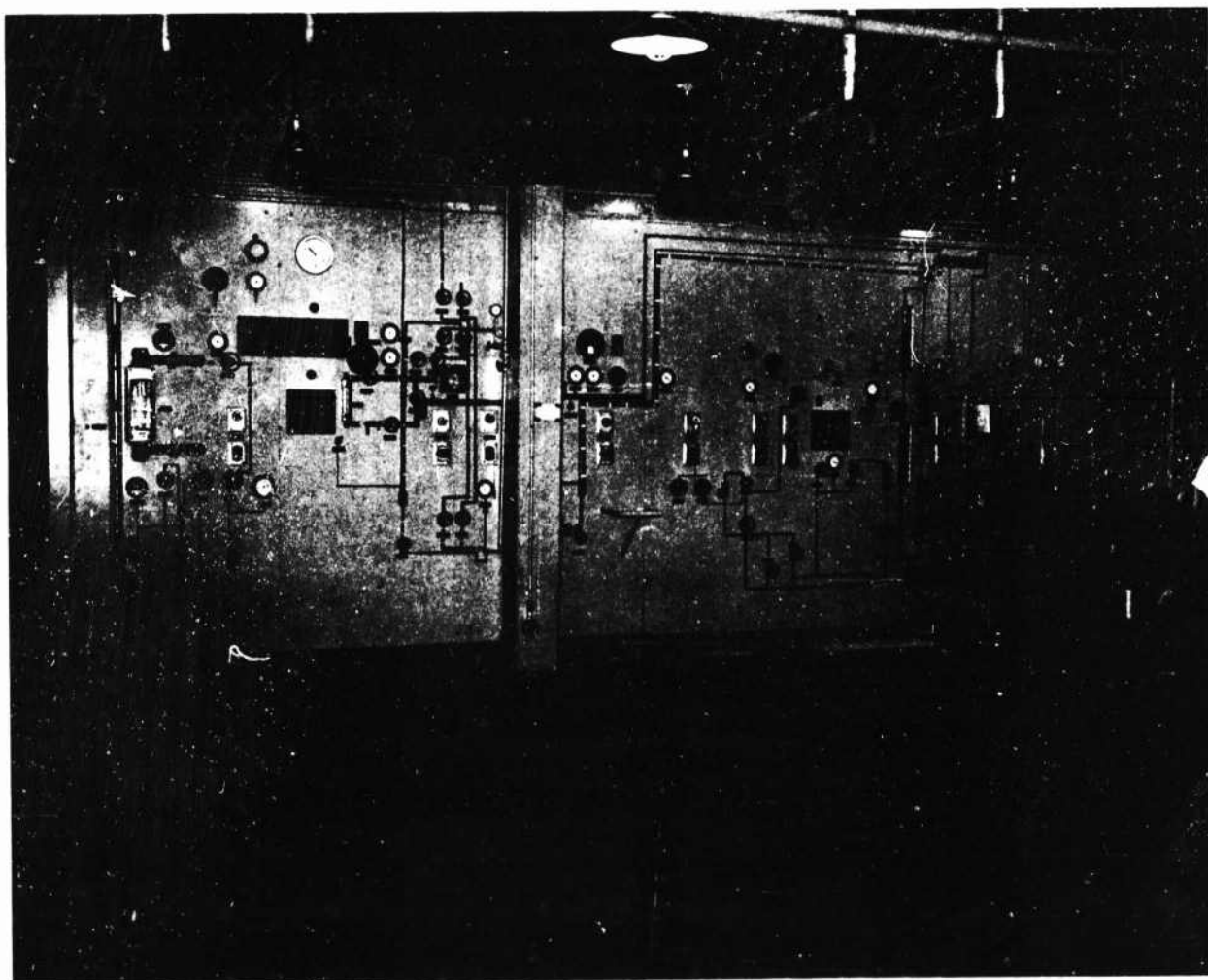


FIGURE 5. AFN PREPILOT PLANT
CONTROL PANEL

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this unit, controlled volumes of the borohydride feed solution and boron trichloride were introduced concurrently at one end of the screw. The diborane and the suspension of sodium chloride in DTG move in parallel flow through the entire length of the reactor. Diborane left the unit as gaseous product, while the spent liquor overflowed from the end plate directly into the receiver.

Diborane leaving the reactor system passed through a cold trap (E-2) maintained at -60°C to -80°C by a solvent-dry ice combination, which removed small quantities of higher boiling impurities. The gas stream was then sampled continuously to a chromatographic automatic stream analyzer and was ready for controlled feeding to the pyrolysis section.

No attempt was made to store diborane as an intermediate; rather it was fed to the pyrolysis section as fast as generated. However, the spent liquor tank (T-7) was an integral part of the generating system and provided a ballast to smooth out any minor variations in generating rate. While the equipment was designed to permit the continuous generation of diborane over prolonged periods of time, the usual practice was to end the run when the sodium borohydride from a particular Step II batch was exhausted.

Process temperatures and pressures throughout the diborane generation system were nominal, i.e., 10 to 15 psig, 30°C to 50°C .

III. Modified Process

The improved diborane process was incorporated into the pilot plant by modifying the equipment used in the previous process and by adding new equipment. The flowsheet for the modified process is presented in Appendix A as Flowsheet B. These changes and additions were made to allow operation of either the previous or the revised process. A description of the modified process follows.

Sodium hydride in a 25 per cent mineral oil dispersion, as produced in the sodium hydride reactor (R-1), was pumped into the 500-gallon Pfaudler stainless steel jacketed reactor (R-2). Recycle solution (Ansul Ether E-141 and mineral oil) from outside storage tanks (T-2, T-3, T-4) was introduced into reactor R-2 to make up the process solution. Addition of boron trichloride to the reactor followed. Manifolding of the boron trichloride supply was modified to permit metering this material as either a gas or liquid.

The reaction of boron trichloride with sodium hydride produced sodium borohydride as a main product. However, small quantities of diborane could be generated during this reaction. A back pressure regulator and line venting the reactor R-2 to the diborane absorption unit (T-9) was

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added to adequately vent any gas produced. Because the reaction in R-2 was highly exothermic and cooling capacity of the reactor jacket was insufficient, an auxiliary water chiller (E-35) with 7.5 tons of cooling capacity was added. This chiller cooled a water-methanol solution which was pumped to the slurry chiller (E-34). The slurry chiller in turn cooled the reaction slurry from R-2. A new slurry circulating pump (P-21) of 40 gallons per minute capacity with double mechanical seals was installed for circulation of the slurry to the chiller and back to the reactor R-2.

The sodium borohydride slurry was transferred to the feed tank T-5 for feeding into the diborane generator R-3. A new Milton Roy feed pump with double ball checks on the inlet and outlet was used to do this. Its capacity was 1 to 10 gallons per minute. To minimize plugging of the slurry lines, Jamesbury ball valves were used in the feed line and pumping circuit. A graduated Pyrex glass tube was used for calibration of the pumping rate. Boron trichloride was fed into the diborane generator (R-3), along with the borohydride slurry, to produce diborane. The spent slurry then passed by gravity to the spent solution tank T-7. From this tank, the slurry was pumped to the centrifuge (K-3) for filtration. A 5 h.p., 40-gallon per minute Peerless pump with double mechanical seals was obtained to accomplish this transfer. Filtrate from the centrifuge was transferred to one of the 500-gallon storage tanks (T-3 or T-4) for recycle and reprocessing.

Because almost all the solutions pumped were slurries or dispersions, double mechanical seals were used to overcome sealing problems. In order to keep the mechanical seals supplied with sealant, individual seal pots or a central sealant distribution system could be used. The previous process used individual seal pots because of the necessity of using several different sealant fluids. However, the new process could be operated with one sealant, mineral oil, to all but two of the mechanical seals. An appreciable manpower savings was achieved by installing a central system which fed sealant to ten mechanical seals in a closed system.

The major equipment of the central sealant system consisted of a 35 gallon carbon steel tank (T-101) equipped with a tubular sight glass, a bronze 15-gallon per minute pump (P-101), and an in-line double pipe heat exchanger in the return line to the tank. Flowmeters on individual mechanical seals were used to detect abnormal usage of sealant.

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LABORATORY SUPPORT

I. Sodium Hydride

Occasionally, batches of sodium hydride produced in the prepilot plant were not of satisfactory quality, often without any apparent reason. These batches were dark gray to black in color, higher in viscosity, perhaps gelled, and usually took up substantially less than the theoretical amount of hydrogen. Therefore a short laboratory investigation was undertaken utilizing prepilot plant raw materials.

A series of three laboratory runs were made in glass equipment which permitted visual observation of the reaction mixture. The sodium hydride products from both plant and laboratory scale operations were compared visually and microscopically.

Deliberate steps were taken to prepare a "black batch" on laboratory scale and the corresponding plant run also produced a black product. Observation of the laboratory scale operation indicated that the sodium dispersion darkened at temperatures in excess of 200°C, prior to the introduction of hydrogen.

On the assumption that the oleic acid used was at fault, plant and laboratory scale runs were made without it. Both operations produced products of satisfactory quality.

Since small amounts of a dispersing agent were sometimes needed in prepilot plant batches to reduce the agitator load, it was recommended that pure oleic acid, purchased in small containers, be substituted for the technical grade oleic acid previously obtained in five gallon cans.

II. Sodium Borohydride

At the start of the prepilot plant investigation, several batches of low purity, off-color sodium borohydride were produced. This problem was also considered in the laboratory.

Low purity borohydride was used to generate diborane in laboratory apparatus. The impurities apparently did not affect diborane generation.

A substantial improvement in color was realized by slurring carbon black and Celite in a solution of the borohydride in Ansol Ether 181, and recovering the borohydride solution by filtration. However, the rate of filtration was extremely slow.

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III. Salt Separation

When boron trichloride was used to neutralize sodium methylate in the regeneration step, a stable suspension of very fine, about one micron, sodium chloride crystals was formed. It was not possible to remove this salt efficiently in the prepilot plant centrifuge. The practice of removing it with a water wash was not commercially feasible because too much methyl borate was lost by reaction with the water.

Several approaches to the problem were tried in the laboratory:

- High speed centrifugation
- Particle size control
- Addition of a fourth liquid
- Distillation
- Filtration

Only the last two appeared to offer an acceptable solution. High speed centrifugation tests with the De Laval Corporation, Precision Scientific Company, and Sharples Company machine yielded slurries with unacceptably low solids content (25% maximum).

Attempts to control sodium chloride particle size by lowering reaction temperature and the rate of boron trichloride addition were not successful. A temperature of 40°C produced no noticeable change in particle size. Although a slight particle size increase was obtained by lowering the boron trichloride addition rate, the increase was not sufficient to affect filtration characteristics.

Flocculation experiments were tried with 17 different agents. Only one of these, Tergitol NP-35, produced an improvement in filterability. Since it is doubtful that it could be either removed from the system or tolerated in the recycle stream, it also was rejected.

The addition of a fourth liquid, cyclohexane, to a partially distilled slurry made it possible to separate the salt by filtration and thus increase the recovery of solvent. However, the resulting mixed solvent would have to be processed to remove the cyclohexane.

A straight distillation of the THF-TMB fraction of the neutralized medium was carried out in a conventional distillation apparatus equipped with a stirrer. The results of this test appear in Table 1.

Heat was slowly applied to this mixture by means of a heating mantle. In a later distillation, the mixture was heated rapidly by placing it in an oil bath at 120°C. The final temperature of the cake was 105°C. The pot residue was honeycombed after nearly 97 per cent recovery of the estimated THF-TMB content, indicating that slow heating may allow collapsing

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TABLE 1

Distillation of NaCl Slurry

Initial Weight of Slurry 538 gms.
Initial Volume 600 ml.
Computed Volume of THF-TMB 486 ml.

ml. Distilled	% of Initial Volume	% Recovery THF-TMB	Temp. °C (Bottoms)	Observations of Pot Contents
153	25.6	31.4	65-66	Noticeable thickness
215	35.8	44.2	66	Thick paste
251	41.8	51.5	66	Pores in cake
302	50.4	62.2	66	Thick cake around sides
327	54.5	67.4	68	
354	59.0	72.8	70	
370	61.7	76.0	98	Agitator stuck
387	64.5	79.5	98	Added 30 ml. oil
404	67.4	83.0	120	Very slow take-off
420	70.0	86.4	160	
425	71.7	87.5	160	Ended distillation

of the oil-sodium chloride residue to trap much of the unrecovered volatiles mechanically. It should thus be possible, in principle at least, to recover nearly all of THF-TMB from the salt slurry by distillation. However, the prepilot plant recoveries were only 80 to 90 per cent due to equipment limitations.

A successful filtration test was conducted at the Walteria Laboratory of the Great Lakes Carbon Company using a vacuum precoat rotary filter testing apparatus. The test results are as follows:

Filter Aid (lbs./100 gal.)	3.5
Drum Speed (rpm)	0.5
Cut (inches)	0.005
Cut (%)	75
Filtration Rate (gpm/sq.ft.)	2.0
Submergence (%)	50
Vacuum (inches Mercury)	22

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The choice of precoat is critical, but with "Speedflow" No. 2 or No. 5, a clear filtrate was obtained, and the filter cake contained 45 per cent of the mixed solvent.

Although distillation was used for salt separation in the prepilot plant as a matter of expediency, filtration would probably be used in a large scale plant. One possible method for recovering solvent from the filter cake is heating the wet cake on a bed of dried recycle salt in a jacketed hollow screw conveyor-dryer. Oil would be recovered from the dried cake by slurrying the cake in water, decanting the oil from the brine, and drying the decanted oil.

IV. Mineral Oil Recovery

The recovery and recycle of mineral oil from the methyl borate-tetrahydrofuran solvent mixture required additional study. It was determined that atmospheric distillation of the solvent away from the mineral oil was effective when aided by nitrogen sparging during the last stages of distillation. The mineral oil could presumably then be cleaned by a filtering system prior to reuse.

Liquid-vapor equilibrium data were obtained for mixtures of methyl borate and tetrahydrofuran. No tendency for azeotropic formation was observed, and the components were difficult to separate by ordinary distillation. Data are given in Table 2 and are shown graphically in Figure 6.

TABLE 2

Liquid-Vapor Data for the System Methyl Borate-Tetrahydrofuran

Sample	Liquid Composition				Vapor Composition			
	Weight Per Cent		Mole Per Cent		Weight Per Cent		Mole Per Cent	
	(CH ₃ O) ₃ B	THF	(CH ₃ O) ₃ B	THF	(CH ₃ O) ₃ B	THF	(CH ₃ O) ₃ B	THF
1	27.02	72.98	20.43	79.57	26.08	73.92	19.66	80.34
2	50.92	49.08	41.85	58.15	49.05	50.95	40.04	59.96
3	68.17	31.83	59.77	40.23	63.50	36.50	54.69	45.31
4	82.72	17.28	76.86	23.14	81.37	18.63	75.19	24.81

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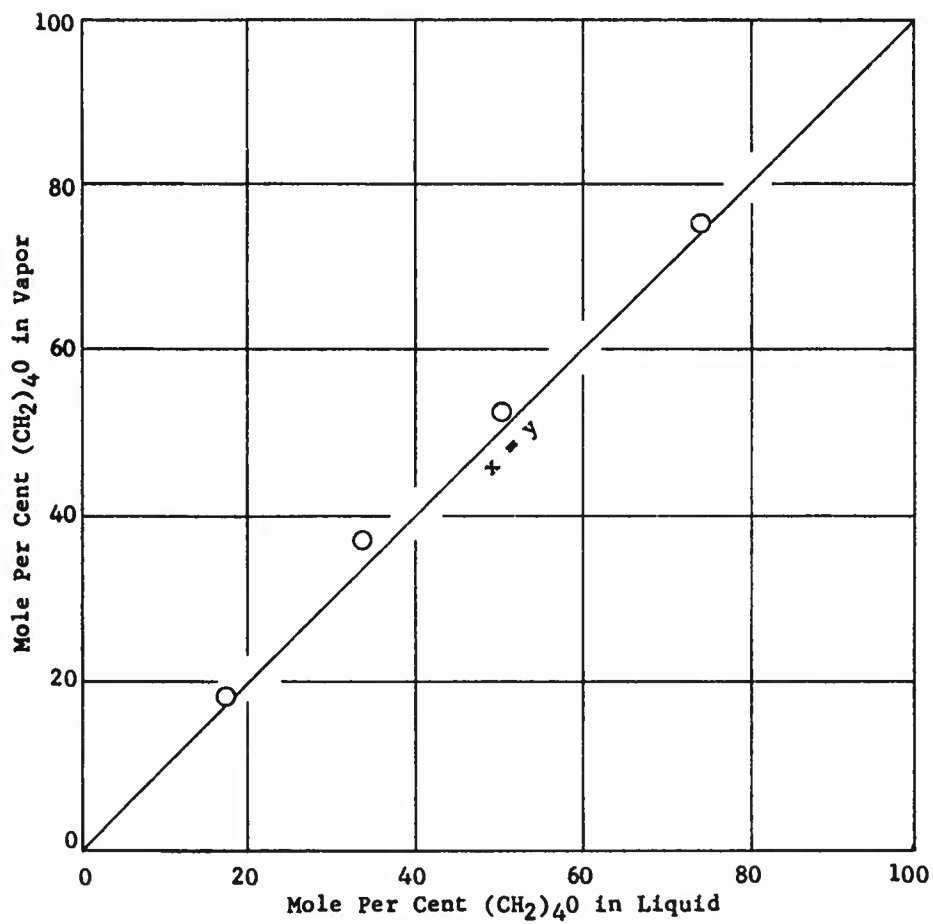


Figure 6. Liquid-Vapor Equilibrium Data
for the System $(CH_3O)_3B-(CH_2)_4O$
One Atmosphere

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The degree of treatment required to make the recovered mineral oil suitable for reuse was also studied. The recycle oil was found to contain impurities arising from cracking during the sodium hydride process, and traces of tetrahydrofuran and water from the boron trichloride neutralization step. These contaminants caused difficulty in obtaining suitable sodium hydride dispersions and pure sodium borohydride.

Simple filtration through filter paper improved the clarity of the oil but the filtrate still was colored and contained water and tetrahydrofuran. By slurring the oil with carbon black (3-5% Darco G-60) and filtering as before, it was possible to obtain a colorless oil with no detectable tetrahydrofuran and an acceptable water content. Oil processed in this way was found suitable for reuse. The analyses of the oils obtained by filtration and filtration with carbon were:

	<u>Simple Filtration</u>	<u>Filtration with Carbon</u>
% H ₂ O	0.082	0.027
% THF	0.02	Not Detected

V. Process Modification

The initial process for producing diborane involved the isolation of sodium borohydride in a relatively pure state and possessed certain disadvantages:

1. The recovery of solid sodium borohydride was sometimes difficult and expensive.
2. The solvents used, trimethyl borate, tetrahydrofuran, and Ansul Ether 181, were expensive and make-up requirements were substantial.
3. Filtration of the sodium chloride which formed in the solvent regeneration step was extremely difficult, if not impossible.

To eliminate these disadvantages, AFN, Inc. developed an economical, one-step process for the production of diborane, based on the direct reaction of sodium hydride and boron trichloride. The sodium borohydride intermediate was used, in situ, according to the following reactions:



The over-all reaction is expressed by:



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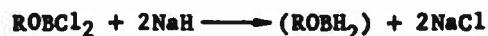
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Laboratory experiments demonstrated that by the addition of boron trichloride to a slurry of sodium hydride in a mixture of mineral oil and Ansul Ether, diborane yields ranging from 73 to 82 per cent could be obtained under the best conditions. The new process removed the need for isolating and drying sodium borohydride, and eliminated the use of trimethyl borate and tetrahydrofuran. It also offered other process simplifications.

The modified diborane process was investigated in the laboratory using the equipment shown in Figure 7. The variables studied were addition of ether, borohydride, fluoride promoters, temperature, rate and amount of boron trichloride addition, and agitation. The results are summarized in Tables 3 through 9.

In Run No. 4 the path of the reaction was followed by infrared analysis of slurry filtrate samples (Figures 8 and 9). In another run the off-gas was analyzed, also by infrared (Figure 10). These curves indicated that sodium borohydride was formed in the liquid phase as long as sodium hydride was available to react with the boron trichloride. Further addition of boron trichloride beyond this point resulted in the acidification of the sodium borohydride in the solution, and the evolution of diborane.

Methyl borate, methyl chloride and methane were identified as side products. Possibly they result from the following reactions, based upon the splitting of the ether by boron trichloride:



These side reactions resulted in a loss of efficiency and in destruction of Ansul Ether in the reaction media.

The primary reactions did not proceed as outlined if impure sodium hydride or boron trichloride were used. It was also found that the additions of promoters, such as Ansul Ether and sodium borohydride, were required. The addition of boron trifluoride or sodium fluoborate were also found highly desirable.

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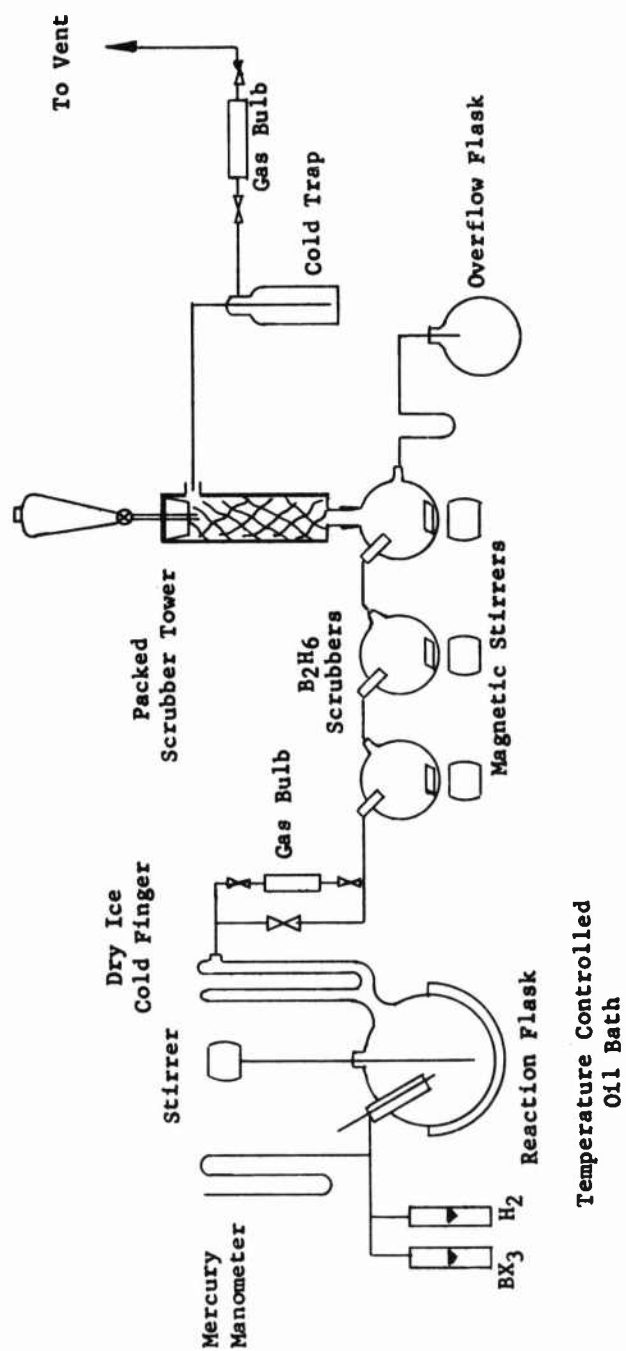


Figure 7. Laboratory Apparatus - Modified Process

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TABLE 3

Reaction Conditions - Modified Process

Run No.	Initial Slurry Make-Up						BCl ₃ to Reaction		Reaction Temp. (°C)	Addn. Rate (g./hr.)
	NaH (g.)	Mineral Oil (g.)	Ansul E-181 (g.)	Ansul E-141 (g.)	NaBH ₄ (g.)	NaBF ₄ (g.)	Added (g.)	Theo. (%)		
1	30.0	90	100.0	-	1.0	-	56.7	114	80	-
2	30.0	-	201.8	-	2.0	-	55.3	109	80	-
3	15.0	45	200.0	-	2.0	-	31.1	118	80	-
4	75.0	-	946.0	-	9.5	-	127.0	110	80	-
5	30.0	270	30.0	-	0.3	-	50.7	103	80	-
6	30.0	270	15.7	-	0.2	-	52.1	106	80	-
7	30.0	270	6.3	-	0.06	-	45.1	91	80	-
8	30.0	-	-	275.2	2.8	-	52.0	101	80	-
9	15.0	-	-	278.0	2.8	-	-	-	25-48	-
10	30.0	270	-	19.4	0.19	-	48.8	100	38-42	-
11	30.0	270	16.4	-	0.16	-	50.3	103	80	-
12	30.0	270	15.4	-	0.15	-	46.9	96	80	-
13	22.5	202.5	31.5	-	0.32	-	39.8	100	80	-
19	24.8	232	-	22.2	0.40	0.9	42.7	105	25	10
20	23.1	227	-	22.2	0.05	0.1	39.8	106	25	10
21	22.5	204	-	23.0	0.46	1.0	38.3	104	25-35	10
22	23.1	228	-	22.5	0.42	1.1	38.3	101	25-35	10
24	22.3	245	23.9	-	0.24	0.6	36.2	100	25-35	10
25	22.4	223	24.4	-	0.24	1.0	36.4	100	25-35	10
26	22.9	243	24.7	-	0.25	1.0	36.2	100	25-44	16.7
27	22.5	228	24.6	-	0.24	1.0	36.7	105	80-95	10
28	22.3	-	-	-	-	1.2	38.0	105	50-55	10
29	23.4	235.1	-	22.5	0.42	1.1	40.4	105	50-55	10
30	23.4	235.1	-	22.5	0.42	1.1	40.4	105	50-60	10
31	23.4	235.1	-	22.5	0.42	1.1	39.8	105	20-35	10
32	23.4	225.1	-	32.4	0.61	1.6	40.5	105	20-35	10
33	23.4	245.1	-	14.4	0.27	0.7	40.1	105	20-35	10
34	23.4	235.1	-	24.4	0.38	-	40.2	105	20-35	10
35	23.4	235.1	-	21.7	0.41	1.1	40.2	105	20-35	15 min. at 26 210 min. at 14
36	23.4	235.1	-	23.6	0.36	1.0	40.3	105	20-35	10

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TABLE 4

Analyses of Solids - Modified Process

Run No.	Solids Analyses							
	Weight Per Cent			meq. x 10/g.			Moles H ₂ per Gram	
	NaCl	Bayol 85	NaBH ₄	NaH	Alk.	Boron	Alk. Hydr.	Acid Hydr.
1	73.5	-	0.36	0.216	0.87	5.67	0.09	0.38
2	90.83	-	1.49	0.24	4.02	5.23	0.1	1.58
3	-	-	-	-	-	-	-	-
4	77.08	-	1.05	0.528	3.31	15.3	0.22	1.11
5	-	75.2	0.388	0.168	1.44	3.5	0.07	0.41
6	14.95	72.6	0.312	3.29	10.9	6.89	1.37	0.33
7	-	-	-	-	-	-	-	-
8	97.92	0.10	0.747	0.168	2.01	2.60	0.07	0.79
9	-	-	-	-	-	-	-	-
10	12.34	-	-	5.66	13.4	8.27	2.36	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
13	68.74	5.28	2.67	14.35	62.6	13.7	5.98	2.82
19	-	11.0	-	-	8.16	7.87	0.49	1.43
20	79.5	2.4	-	-	37.7	9.49	3.60	0.82
21	90.8	-	0.5	0.6	0.92	8.60	0.23	0.52
22	85.9	3.3	0.7	3.4	10.2	9.30	1.42	0.75
23	54.6	3.3	1.0	18.6	48.4	27.0	7.77	1.05
24	63.3	23.5	2.6	1.6	6.11	14.4	0.66	2.75
25	77.9	4.0	1.4	1.7	0.71	11.0	0.70	1.52
26	63.4	17.9	-	-	5.46	13.4	0.58	2.16
26a	68.1	9.5	-	-	11.36	13.4	0.38	1.64
27	67.4	13.2	1.1	1.8	4.61	13.3	0.77	1.22
28	53.1	5.0	-	-	121.9	23.1	11.8	1.0
29	78.5	3.1	0.6	6.1	23.4	11.5	2.54	0.61
30	70.5	3.7	0.5	6.0	20.1	19.8	2.50	0.34
31	82.9	6.3	1.5	0.9	6.0	11.1	0.38	1.73
32	83.4	5.5	0.9	0.7	0.8	10.9	0.28	0.99
33	29.2	3.2	0.2	0.4	213.1	26.9	21.5	0.16
34	67.3	18.9	1.0	2.5	1.39	11.5	0.24	1.04
35	51.1	2.0	1.4	3.7	60.1	35.1	8.55	1.53
36	73.7	13.1	0.4	1.1	-0.38	11.2	0.19	0.45

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TABLE 5

Analyses of Filtrates and Diborane Yields - Modified Process

Run No.	Filtrate Analyses						Diborane Evolved		
	Weight Per Cent					mmoles H ₂ /g. Acid Hydr.	Collected (g.)	Theo. (g.)	Yield (%)
	meq. x 10/g. Alk.	10/g. Boron	Ansul ether	Mineral Oil	Cl				
1	-	-		-	-	-	-	-	-
2	-0.47	13.8		-	-	1.09	-	-	-
3	-	-		-	-	-	-	-	-
4	0.12	8.0		-	nil	0.66	-	-	-
5	nil	0.37		96.9	nil	nil	-	-	-
6	1.65	2.74		91.9	0.81	0.06	-	-	-
7	-	-		-	-	-	-	-	-
8	0.20	7.42		-	nil	1.23	1.19	7.11	16.7
9	-6.6	8.34		-	2.35	1.14	2.21	4.2	52.5
10	-3.20	2.18		-	0.92	0.19	1.15	5.85	19.7
11	-13.4	8.04		-	4.74	nil	1.17	5.84	20.0
12	-20.8	10.9		84.4	7.56	-	0.83	5.84	14.2
13	nil	4.36		90.0	nil	1.75	5.85	5.85	30.0
19	sl. acid	1.01	4.1	60.2	0.02	0.03	3.20	4.97	64.3
20	-0.09	2.13	2.9	92.2	nil	0.02	2.61	4.48	57.2
21	-0.04	0.79	6.2	90.7	nil	0.02	3.49	4.41	79.2
22	sl. acid	0.78	-	-	nil	0.07	3.44	4.64	74.2
23	-0.52	1.28	0.2	97.6	nil	0.03	1.53	4.09	37.4
24	neutral	0.26	3.2	83.2	nil	0.03	2.4	4.29	55.9
25	neutral	0.29	2.6	96.8	nil	0.03	3.3	4.29	76.0
26	neutral	0.21	2.7	-	nil	0.03	2.2	4.3	51.2
27	neutral	0.46	3.3	92.3	nil	0.03	2.6	4.31	60.6
28	-11.0	6.30	-	89.4	4.04	nil	0.81	4.29	18.9
29	neutral	1.29	3.7	89.6	-	nil	2.71	4.70	57.6
30	-0.30	1.44	0.5	92.9	-	0.09	3.07	4.70	65.3
31	neutral	0.66	7.5	89.3	-	0.03	3.44	4.70	73.2
32	neutral	0.63	9.2	86.7	-	0.08	3.61	4.79	75.4
33	-16.4	8.7	0.3	83.5	5.8	nil	nil	4.63	0
34	neutral	0.76	6.22	85.6	nil	0.05	3.42	4.66	73.3
35	-0.40	1.36	< 0.5	88.5	0.18	0.15	0.61	4.67	13.1
36	-	0.66	5.9	89.8	nil	0.07	3.83	4.67	82.0

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TABLE 6

Incremental Analyses of Filtrate - Modified Process
Run 4

Sample and I.R. Curve Number	BCl ₃ Addition Time (min.)	BCl ₃ Added (g.)	Filtrate Analyses			
			meq. x 10/g.		mmoles H ₂ per gram	
			Alk.	Boron	Alk. Hydr.	Acid Hydr.
1	60	19.0	1.23	1.30	0.09	0.47
2	120	38.0	1.64	1.68	0.10	0.52
3	180	57.5	2.33	2.39	0.10	0.88
4	240	76.5	2.67	2.62	0.12	0.98
5	280	89.5	3.08	4.28	0.14	1.19
		Start of rapid diborane evolution.				
6	340	109.0	1.13	5.20	0.16	1.17
7	375	120.0	0.17	5.49	0.15	1.10
8	397	127.0	0.12	8.00	0.16	0.66

TABLE 7

Incremental Analyses of Off-Gases - Modified Process

Elapsed Time % of Total	% of BCl ₃ Added	B ₂ H ₆ Flow cc/min.	B ₂ H ₆ Purity Mole %	CH ₄ Flow cc/min.	CH ₄ Mole (%)	CH ₃ Cl Flow cc/min.	CH ₃ Cl Mole (%)	Reactor Temp. (°C)
13.0	17.6	-	-	9.78	98.5	0.14	1.5	25
21.6	29.3	-	-	11.85	98.5	0.19	1.5	25
37.8	50.9	2.11	15.0	11.72	83.3	0.23	1.7	25
42.2	56.8	24.25	56.2	18.39	42.6	0.48	1.2	25
53.0	71.7	2.82	40.0	3.78	53.5	0.45	6.5	25
55.0	76.6	5.75	68.25	2.67	31.75	-	-	25
61.0	86.3	46.63	93.54	3.07	6.16	0.15	0.3	25
70.5	94.9	79.17	96.74	1.39	1.69	1.28	1.57	25
74.0	100.0	178.75	97.5	1.67	0.91	2.92	1.59	25
91.5	-	26.05	93.92	0.79	2.85	0.90	3.23	75
100.0	-	33.04	89.60	2.10	5.70	1.73	4.69	100

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TABLE 8

Make-Up and Diborane Yields - Modified Process
(Dry Sodium Hydride)

Run No.	14	15	16	17	18
<u>Temperature (°C)</u>	80	25-30	80	13-18	-5 to 5
<u>Starting Slurry (g.)</u>					
NaH	22.5	22.5	22.5	22.5	22.5
E-141 Soln.	244	237	262	243	242
<u>E-141 Solution</u>					
<u>Composition (wt. %)</u>					
NaBH ₄	1.89	0.95	1.16	1.16	0.88
NaBF ₄	4.36	1.62	4.36	4.36	4.06
<u>BCl₃ Added (g.)</u>	41.3	40.7	41.7	42.5	41.1
<u>B₂H₆ Evolved (g.)</u>	1.61	2.99	3.33	4.27	3.46
<u>Efficiency</u>					
<u>(%, based on B₂H₆)</u>	24.5	40.7	57.3	74.8	64.5
<u>Final Slurry</u>					
<u>Weight (g.)</u>	291	296	321	300	298

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TABLE 9

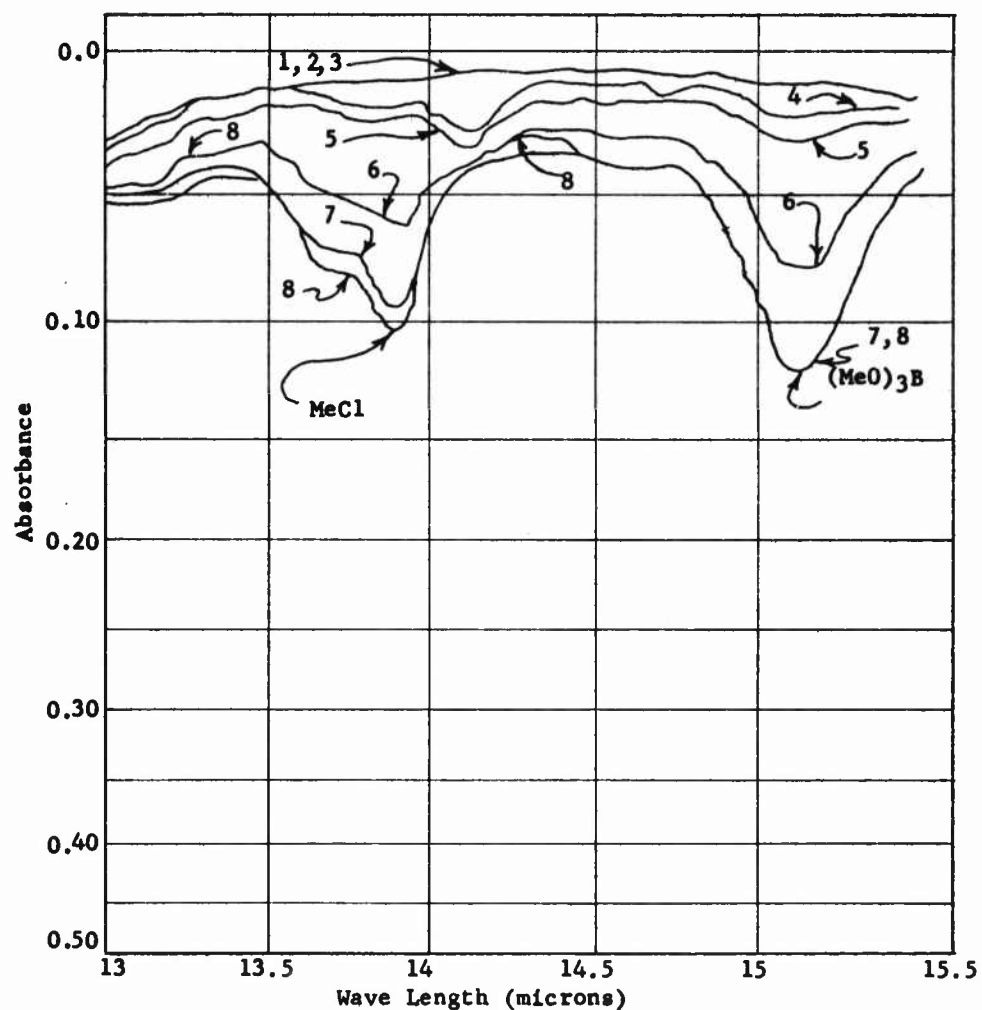
Analyses of Solids and Filtrates - Modified Process
(Dry Sodium Hydride)

Run No.	14	15	16	17	18
<u>Filtrate</u>					
Weight (g.)	205	219	255	218	228
Alk., meq. x 10/g.	0.8	-6.6	-2.9	-3.8	-4.4
Boron, meq. x 10/g.	5.42	5.43	11.0	9.26	8.53
Alk., mmoles H ₂ /g.	nil	0.12	0.13	0.09	0.08
Acid, mmoles H ₂ /g.	0.29	0.39	0.14	0.07	0.03
F, (wt. %)	2.69	1.62	3.33	3.18	2.35
<u>Dry Solids</u>					
Weight (g.)	86.4	77.0	66.4	82.0	69.5
Alk., meq. x 10/g.	0.62	sl. acid	0.62	-1.8	neutral
Boron, meq. x 10/g.	6.41	1.51	2.0	3.52	1.9
F, (wt. %)	1.41	0.72	0.47	1.16	0.56
Alk., mmoles H ₂ /g.	0.06	0.02	nil	0.04	0.04
Acid, mmoles H ₂ /g.	0.81	0.13	0.39	0.09	0.24
NaCl (wt. %)	68.7	73.7	88.5	72.5	84.7

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Figure 8. Liquid Phase Infrared Absorption Spectra
Modified Process, Run 4



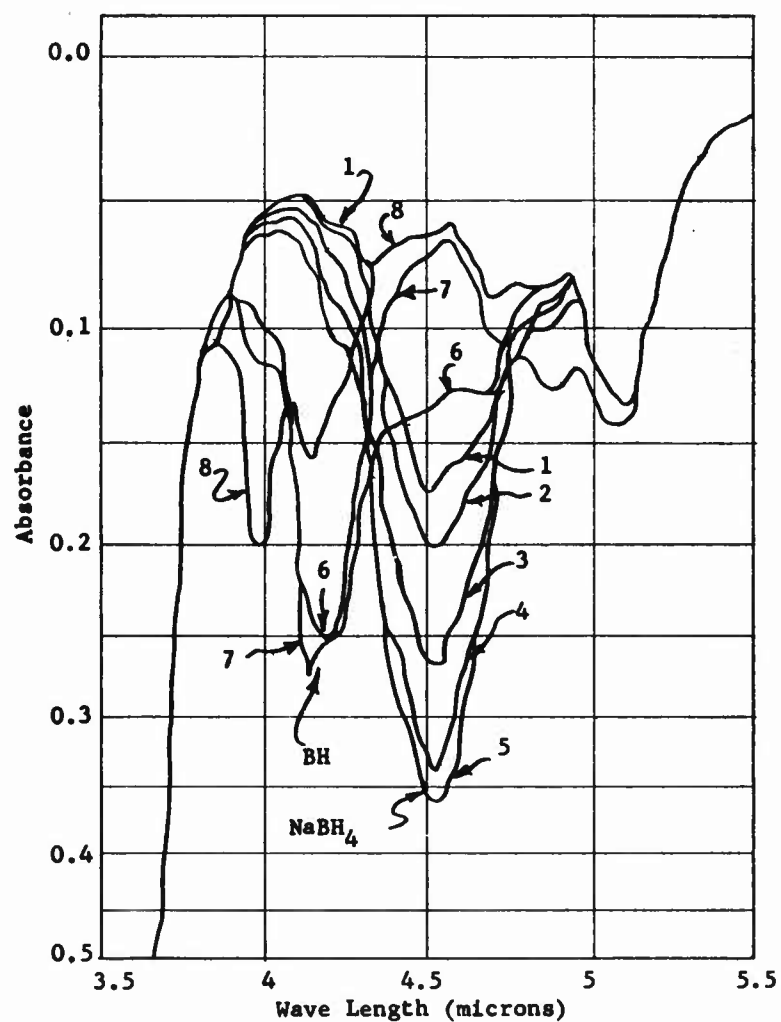
Note: Numbers refer to
increments of boron
trichloride addition

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Figure 9. Liquid Phase Infrared Absorption Spectra
Modified Process, Run 4



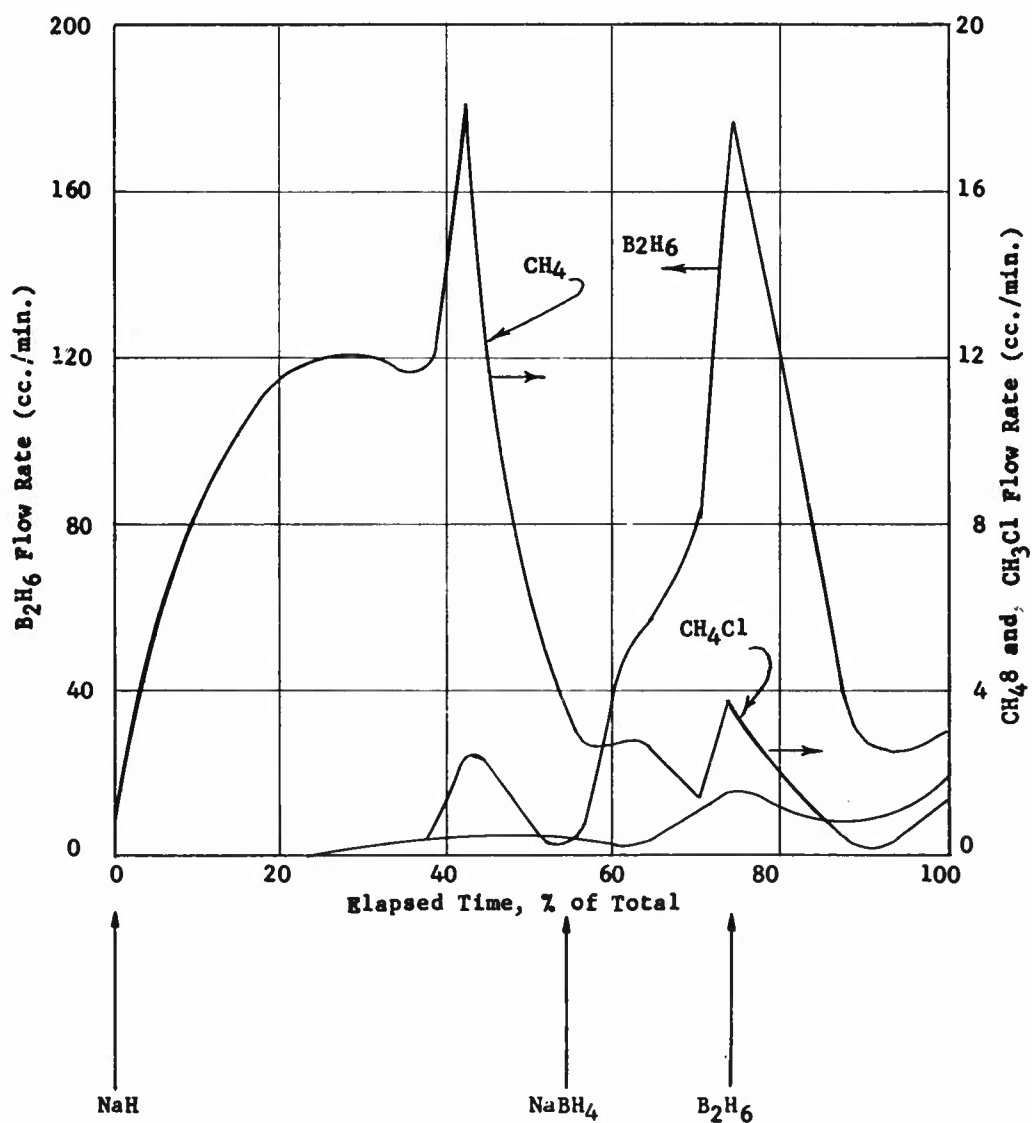
Note: Numbers refer to
increments of boron
trichloride addition

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Figure 10. Off-Gas Composition - Modified Process
(Incremental Addition of BCl_3)



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Both Ansul Ether E-181 (tetraethylene glycol dimethyl ether) and E-141 (diethylene glycol dimethyl ether) were used in the reaction and both were effective. However, E-141 was found to be more stable and produced a much less viscous slurry than E-181. A minimum of about five per cent ether in the hydride slurry seemed to be required for the reaction. Although increasing the ether concentration above this value improved the yield, the increase was small.

An initial concentration of 0.2 per cent sodium borohydride in the hydride slurry seemed adequate to promote the reaction. The addition of small amounts of either sodium fluoborate (in the slurry) or boron trifluoride (in the boron trichloride feed) was also highly desirable, since the reaction proceeded much more smoothly, gave better yields, and produced a more readily filtered sodium chloride slurry.

The effect of reaction temperature on yield was investigated over the range of 5°C to 80°C, and 15°C was found to be optimum. However, at the end of the boron trichloride addition, the slurry was heated to about 100°C to complete the reaction and drive off dissolved diborane.

The following is typical of the laboratory preparations.

One hundred forty nine grams (149 g.) of Ansul Ether E-181 containing 1.5 grams of sodium borohydride were placed in the reaction flask and 15 grams of sodium hydride were added. In the diborane absorption flask were placed 144 grams of a solution of sodium methylate in methyl borate and tetrahydrofuran, containing 8 per cent sodium methylate and 46 per cent methyl borate. The entire system was then swept with nitrogen, and the oil bath under the reaction flask was heated to 80°C. The absorber liquor was heated to 35°C. With both flasks being rapidly stirred, boron trichloride was added to the reaction flask at approximately 12 grams per hour while a nitrogen sweep was maintained. At twenty minute intervals a gas sample was taken and the boron trichloride cylinder weighed to ascertain the exact amount of boron halide added. A sharp rise in the diborane concentration was noted in the gas sweep between the fifth and sixth additions, when approximately the theoretical weight (18.3 g.) of boron trichloride had been added. No free sodium hydride was evident in the slurry of white solids present at the end of the fifth addition, and no solids were present in the scrubber.

Further additions of boron trichloride were made and gas evolution was evidenced by the bubbling and foaming of the slurry. Boron trichloride was then added in slight excess of that required to neutralize all the sodium borohydride. The reaction slurry was then cooled and centrifuged, and the filtrate decanted. The wet solids were washed, first with Ansul Ether, then with tetrahydrofuran, and finally dried under vacuum. Thirty-eight grams of dried solids were obtained (theoretical yield of sodium chloride, 38.8 g.).

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VI. Analytical Procedures

Analytical coverage for the various steps of the prepilot plant operation and the associated laboratory investigations necessitated the development and use of a considerable number of analytical procedures. In most cases, new procedures had to be developed specifically for the materials in question so that meaningful analytical results could be obtained for evaluating the performance of the prepilot plant and of various associated laboratory projects. The toxic nature of the boron hydrides made special safety precautions necessary. In particular, the handling of the volatile boron hydrides necessitated the construction of special vacuum apparatus and required training of laboratory personnel in vacuum techniques. Care was exercised in working with samples containing sodium, sodium hydride and sodium borohydride because of the possibility of hydrogen ignition upon hydrolysis.

The various types of analytical work (developmental and routine) carried out during the period of laboratory and prepilot plant operation consisted of (1) chemical analyses, (2) infrared analyses and (3) miscellaneous analytical projects.

A. Chemical Analyses

1. As expected, the determination of boron in the various boron containing compounds and solutions was of considerable importance. Boron in soluble borates was determined by simply adding mannitol to an aliquot of the neutral, unbuffered solution and titrating with standard alkali to a phenolphthalein endpoint, or to a pH of 8.0 when a pH meter was used. Total boron present in Ansul Ether-sodium borohydride feed, in spent solutions and in filter cakes, was determined by hydrolyzing the sodium borohydride and other compounds present to boric acid and titrating with standard base in the presence of mannitol. Hydrochloric acid converted the sodium borate to boric acid which was then titrated with standard sodium hydroxide in the presence of mannitol to obtain the total boron content.

Attempts by prepilot plant personnel to obtain material balances on the process indicated that the boron values obtained in caustic scrubber solutions were generally low. Procedures undertaken to correct this problem included:

- a. Direct titration of the sample.
- b. Evaporation of a sample to dryness and fusion of the resulting solids with sodium carbonate.
- c. Filtration of the sample solids with subsequent fusion of the solids and standard titration of the liquid portion.

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These procedures proved unsatisfactory due either to incomplete conversion of the boron to the plus 3 state, or to the extreme lengthiness of the procedure. A perchlorate oxidation of these caustic scrubber solutions was later successful. The method was based on the conversion of all boron to soluble boric acid by heating with nitric and perchloric acids followed by the standard mannitol-sodium hydroxide titration. This procedure was comparatively rapid and yielded reproducible results. The values obtained were approximately double those obtained by the direct titration technique for polymer destruction liquors. This investigation showed it was unnecessary to determine the boron contained in the final destructive scrubber solutions by the perchlorate oxidation procedure since comparable results were obtained by direct titration.

2. A mixture of trimethylborate and tetrahydrofuran was used in the production of sodium borohydride from sodium hydride. Three procedures were employed to determine the percentage of trimethylborate in tetrahydrofuran: specific gravity, refractive index, and hydrolysis to boric acid with titration neutralization of the acidity from the boric acid-mannitol complex. Instructions and equipment were prepared and turned over to the prepilot plant personnel for the specific gravity method. This made possible rapid, on-the-spot analyses.

3. The sodium hydride produced in Step I was analyzed for purity by the decomposition of sodium hydride and free sodium with isopropanol and water to yield sodium hydroxide and hydrogen. A gas burette was used to determine the volume of hydrogen evolved. The reaction mixture was then titrated for total alkalinity. Calculations for the per cent sodium and sodium hydride utilized the volume of hydrogen evolved and the alkalinity, with the aid of the following equations:



In the absence of free sodium, the per cent sodium hydride was calculated from the volume of hydrogen alone, based on the first equation, or from the alkalinity. The method was applicable to both sodium hydride solids and their dispersions in mineral oils.

Considerable skill on the part of the analyst was required, especially if sodium was present. The slightest variation in procedure could lead to unusual results.

4. Sodium methylate appeared in Step II as one of the products in the reaction of sodium hydride with trimethylborate, the other product

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being sodium borohydride. The filtrate from the sodium borohydride recovery was analyzed for sodium methylate by hydrolysis to sodium hydroxide and methanol, followed by titration with standard acid to determine the alkalinity produced.

5. Since mineral oil was used as the dispersion medium for sodium hydride, it was a natural contaminant of the sodium borohydride produced. Mineral oil was determined in sodium borohydride process materials by its extraction with dichloromethane from an acidified aqueous solution of the sample. Dichloromethane was evaporated and the mineral oil residue dried and weighed. This method was applicable to the determination of the mineral oil content of samples of sodium borohydride, sodium fluoride, sodium chloride, and solutions of these materials in Ansul Ether, methyl borate, tetrahydrofuran and water. Any material extractable with dichloromethane but which did not evaporate below 110°C interfered with the method.

6. Samples of boron trichloride were analyzed for silicon and free chlorine colorimetrically after alcoholysis and hydrolysis. A liquid sample of boron trichloride was distilled into methanol and water was added to hydrolyze the resulting methyl borate to boric acid and the silicon to silica acid. An aliquot of this solution was analyzed for chlorine by the o-tolidine colorimetric method. Silicon was determined colorimetrically by either the silico-molybdate method (over 25 ppm Si) or the molybdenum blue method (below 25 ppm Si). Both the overhead and residue from the distillation were analyzed for silicon by one of these two methods. These chemical methods are outlined in detail in Appendix B.

B. Infrared Analyses

The infrared spectrophotometer (Beckman IR-4) was extremely useful in providing analytical services during laboratory and prepilot plant operation. Methods were developed for the quantitative analysis of (1) tetrahydrofuran in mineral oil, (2) sodium borohydride in Ansul Ether 181, (3) Ansul Ether 141 in mineral oil, (4) boron trichloride in gas samples, and (5) phosgene in gas samples. The instrument was also very useful for the qualitative identification of these and other compounds. It provided rapid analyses and did so with small samples that were not chemically altered during the analysis.

1. The tetrahydrofuran content of mineral oil was determined by filling a 0.1 mm. liquid cell, measuring the absorbance obtained by single beam point analysis at 9.31 microns and referring to a previously obtained calibration curve of absorbance versus volume per cent tetrahydrofuran. The analytical range was 0.05 to 1.0 gram tetrahydrofuran per 100 milliliters.

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2. The sodium borohydride content of Ansul Ether 181 was determined by filling a 0.03 mm. cell, scanning the sample between 6 and 2 microns, measuring the absorbance at 4.48 microns, and referring to a previously obtained calibration curve of g.NaBH₄/100 ml. versus absorbance. The analytical range was 0.01 to 8.0 g. NaBH₄/100 ml.

3. The Ansul Ether 141 content of mineral oil was determined by filling a 0.0264 mm. liquid cell, measuring the absorbance at 8.97 microns, and referring to a previously obtained calibration curve of weight per cent Ansul Ether 141 versus absorbance. The analytical range of the method was 0 to 15 grams Ansul Ether 141 per 100 milliliters.

4. The boron trichloride content of a gas sample was determined by filling a 10 cm. gas cell to a known pressure (high vacuum system necessary) and then obtaining the double beam IR spectrum of the gas. The absorbance of boron trichloride was measured at 5.22 microns for high concentrations, or at 10.06 microns for low concentrations. Calibration curves for each wave length were available for determining the partial pressure of boron trichloride. From the partial pressure the mole per cent boron trichloride was easily calculated.

5. The phosgene content of a gas sample was determined by filling a 10 cm. gas cell to a known pressure (high vacuum system necessary) and then obtaining the double beam IR spectrum of the gas. The absorbance of phosgene was measured at 11.77 microns. A previously prepared calibration curve was available for determining the partial pressure of phosgene in the sample. The mole per cent could be easily calculated from the partial pressure.

These infrared methods are detailed in Appendix B.

C. Miscellaneous Analytical Projects

1. A high frequency analyzer was fabricated and installed in the prepilot plant for use in monitoring Step II solutions. Two coils were prepared for use with the analyzer. One, a large coil, was placed on a section of glass pipe through which the reaction mixture, in the sodium borohydride reactor (R-2), could be circulated. A smaller second coil was used with test or culture tubes of 15 mm. length and some 20 mm. O.D.

Instrument calibration for the sodium methylate neutralization through the preparation of synthetic standards was unsuccessful due to inability to prepare a set of standards having physical characteristics

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similar to the plant solutions. It was found that the instrument could be used to estimate the nearness of completion of the neutralization to an endpoint within 4 grams per liter of neutral.

The instrument proved to be more useful in determining the free sodium content of the sodium hydride slurries fed to Step II. A set of standards ranging from 0.1 to 5.1 per cent sodium was prepared in sealed test tubes and a calibration curve obtained with the small coil. Both the standards and the calibration curve were made available to prepilot plant operators who then could make their own determinations on samples of sodium hydride slurries.

The high frequency analyzer greatly increased the ease with which the aforementioned processes could be followed analytically, and resulted in considerable time saving.

2. Identification of the impurities present in sodium borohydride was desired to enable the prepilot plant personnel to establish the origin of contaminants in the product. Accordingly, a study was initiated to determine the nature of these impurities. Sodium tetramethoxyborate was the principal contaminant identified in average batches of sodium borohydride (> 90% purity). This accounted for from 3 to 7 per cent of the sample. The other contaminant appeared to be a boron containing compound, probably B_2O_3 or a borate. Batches of lower purity sodium borohydride had more sodium tetramethoxyborate. The ratio of sodium tetramethoxyborate to other impurities, however, was not so high as that noted in the purer material. This was probably due to more mineral oil or in some cases to carbon (charred mineral oil). In this investigation, methoxy groups were determined by hydrolysis to methanol, distillation of the methanol, and finally oxidation of the methanol in the distillate with standardized ceric nitrate solution. Then, using ferroin indicator, the excess ceric ion was titrated with 0.1 N arsenous oxide until a permanent pink color was obtained. Boron and alkalinity values were determined by hydrolysis of the sodium borohydride followed by standard titrations with 0.1 N sodium hydroxide and 0.1 N hydrochloric acid. Mineral oil values were determined by extraction with dichloromethane as previously described.

3. Diborane was produced in the prepilot plant through the reaction of sodium borohydride with boron trichloride. A possible reaction between diborane and sodium borohydride was investigated since this reaction might adversely affect diborane production. Little or no reaction was found to take place between diborane and sodium borohydride, either in solid form or slurried in Ethyl Ether. Diborane was found to react rapidly with sodium borohydride in Ansol Ether 181 to yield large quantities of hydrogen and sodium-boron-hydrogen compounds containing

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more than one boron atom. This reaction was of interest not only because it was detrimental to diborane production but because it could possibly open the door for the synthesis of other boron hydrogen compounds. The urgency of other more pressing projects necessitated the discontinuance of work on this reaction.

4. A study was made to determine the amount of low boiling material (boiling point below that of Ansul Ether 141) present in filtered spent solutions after diborane generation. Values of slightly less than 2 per cent by weight were obtained by distillation of filtered spents from several runs. Infrared analysis of the low boilers indicated structure types similar to that of Ansul Ether 141. The low boiling material was thought to be fragments of Ansul Ether 141 produced by the reaction of boron trichloride with Ansul Ether. The presence of this material in the filtered spent biased high the results obtained in the infrared determination of Ansul Ether 141. This bias was eliminated in those instances where precise Ansul Ether values were necessary by quantitatively distilling off the low boilers before performing the IR analysis.

PREPILOT PLANT OPERATIONS

I. Discussion

A. Sodium Hydride (Step I)

The first 34 batches of sodium hydride were initiated for use in the methyl borate process for sodium borohydride production. As indicated in Table 10, 33 of these batches were carried through the hydride step. Batch No. 10 was discarded prior to hydriding because the sodium dispersion obtained was very coarse, in the order of 200 micron particle size, despite the addition of extra dispersing agent (oleic acid) and an extra long dispersing period. It was suspected that the batch had somehow become contaminated and probably would not hydride satisfactorily. Since disposal of a poor hydride batch, along with the necessary clean-up of equipment, was particularly time consuming it was decided to restart. Batch No. 11 proceeded very well and proved the decision correct.

Preliminary laboratory experiments had demonstrated that certain factors, e.g., too high a temperature or too much dispersing agent, can result in a "black batch". In this circumstance, the oil (or the dispersing agent) carbonizes, lending a color varying from dark gray to opaque black to the product slurry. Such a batch does not absorb hydrogen readily; in fact, it usually ceases hydrogen uptake far short

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of the theoretical quantity. Despite the forehand knowledge of this subject acquired in the laboratory, some of the batches prepared in the pilot plant were unsatisfactory. Experience with the early batches proved that high quality sodium hydride was necessary if the subsequent processing to sodium borohydride in Step II were to proceed smoothly and yield a good product. Again, because operating difficulties with a poor sodium borohydride batch far exceeded the effort required to start over, it became the practice to discard a questionable batch. Thus, sodium hydride Batches 7, 13, 14 and 34 were not used.

Batches 35 through 86 were prepared for the "in situ" process for making sodium borohydride. At this time, the Air Force asked that a minimum of effort be put into the steps leading up to the pyrolysis of diborane. Since no basic changes were made in the sodium hydride process and because the data presented in Table 10 are typical of the later batches as well, only special comments are tabulated for Batches 35 through 86 in Table 11.

With the exception of Batch 42, which was interrupted when cooled excessively, Batches 35 through 57 hydrided smoothly and produced sodium hydride dispersions containing less than 0.1 per cent free sodium. A wide range of oil mixtures was used in that the percentage of reprocessed oil, i.e., oil recovered from subsequent steps, was varied from 0 to 100. In addition, various grades of mineral oil were used and found satisfactory: Penola Bayol 85, Standard No. 3 NF, and White Oils Nos. 10 and 15 (Mefford Chem. Co.).

Erratic results were experienced with Batches 58 through 68. Batch 58 was inadvertently started on top of Batch 57 which had not yet been used in Step II and was, therefore, still in Reactor R-1. This overloaded the agitator and its blade was damaged. The batch turned out dark and was discarded. Reactor washout and agitator repair followed, but results were inconsistent for the next several batches. With Batch 69, normal results were obtained and the last 18 batches were processed uneventfully.

The occurrence of occasional unsuccessful batches caused concern. Formulations and operating procedures for all batches were carefully reviewed; however, no single factor could be pinpointed as a cause. A brief laboratory program, discussed earlier, was undertaken to help clear up this matter. It was concluded that the technical grade oleic acid used in the pilot plant was unsatisfactory, probably because of deterioration over several months. Batches 69 through 86 either used no oleic acid or only small amounts of C.P. grade material. The sodium dispersion before hydriding was usually very coarse and, in fact, often agglomerated when sampled; nevertheless, hydriding proceeded normally.

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TABLE 10
STEP I. PREPILOT PLANT BATCHES 1-34
(Sodium Dispersion, Sodium Hydride)

BATCH NO.	USED Na (LBS.)	Na HEAT UPTIME (HRS.)	SODIUM DISPERSION TIME (HRS.)	PART. SIZE (μ)	VESSEL PRESS. (PSIG) (AVG.)	MAX. H ₂ FLOW SCFM	HYDRID. TIME (HRS.)	HYDRID. TEMP. (°C)	THEOR. H ₂ USED (%)	TOTAL CYCLE TIME (HRS.) ^(a)	FREE Na IN NaH (%)
1	105.0	1.0	0.7	-	35	6.3	5.1	275	101	8.0	4.0
2	107.5	1.5	0.3	-	35	3.8	10.6	270	86	12.0	1.5
3	105.5	2.0	0.5	-	37	5.8	10.2	260	78	27.0	0.2
4	106.5	2.0	1.25	30-40	38	8.5	4.4	270	114	11.0	0.2
5	106.0	2.2	0.5	-	35	8.2	4.8	270	106	10.0	0.3
6	108.0	2.4	1.4	-	32	12.5	3.8	270	91	8.0	0.2
7	107.0		0.5	20	38	4.2	14.8	265	Leaky Valves	16.4	-
8	106.0	2.2	0.7	20-40	32	8.7	5.5	250	"	6.7	0.2
9	106.0	4.7	3.0	50-60	34	8.3	4.0	250	131	13.0	0.7
10	106.0	2.4	Discarded								
11	109.0	3.6	3.0	50-100	35	5.5	7.3	270	99	11.0	0.1
12	109.0	3.2	3.1	-	29	11.7	3.0	280	111	8.5	0.1
13	109.0	2.2	2.0	-	31	6.3	4.8	280	100	10.0	2.0
14	110.0	(a)	1.6	5-75	36	5.0	3.6	265	91	7.0	-
15	107.0	6.5	2.6	20-30	40	12.6	7.0	245	108	13.5	0.1
16	107.0	2.4	1.2	20-50	44	13.9	3.0	240	105	5.9	1.0
17	96.0	3.0	1.2	20	44	16.4	1.5	235	104	5.2	0.6
18	108.0	13.0	1.7	10-50	45	15.5	2.7	255	113	5.2	0.1
19	106.0	4.1	2.1	35	46	6.0	5.5	280	104	8.7	0.1
20	107.0	5.5	38.0	70	42	7.0	4.7	265	75	45.5	0.1
21	104.0	4.3	10.9	90	44	4.0	15.4	255	91	28.0	1.1
22	106.5	3.2	2.0	150	40	7.5	3.0	265	104	5.8	0.1
23	108.0	2.0	3.3	110	45	8.0	3.6	260	102	8.0	0.1
24	107.5	3.8	1.7	70	41	6.5	3.7	255	99	6.7	0.1
25	105.5	7.0	2.1	60	42	8.0	3.4	270	102	7.7	2.0
26	107.0	3.2	1.0	60	42	5.8	5.2	260	109	7.7	-
27	107.0	3.7	3.25	20	38	5.5	16.5	265	102	20.5	None
28	103.5	2.7	1.3	150	43	7.6	4.0	255	105	6.25	0.1
29	107.5	3.0	0.75	60	39	6.3	6.5	255	110	7.5	1.0
30	106.0	11.8	3.8	140	41	14.6	9.2	262	140	13.3	0.1
31	105.0	4.0	1.25	50	44	10.5	3.3	259	105	5.1	0.1
32	107.0	2.3	2.1	100	38	5.8	3.5	250	103	6.1	0.1
33	106.5	3.4	1.7	25	42	6.3	4.5	250	105	6.8	0.1
34	105.0	1.9	0.8	50	44	10.5	4.0	260	58	6.5	-

(a) Total cycle time - Start Na addition to 150 °C at finish of Hydriding

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TABLE 11

Step I Prepilot Plant Batches 35-86
(Sodium Dispersion, Sodium Hydride)

Batch Nos.	Comments
35-41	These successful batches utilized varying proportions (up to 100%) of reprocessed oil. Batch 41 is the first one which used a 135 lb. Na drum, i.e., larger batch size.
42	A black batch; discarded. Accidentally cooled too much in middle of hydriding, losing reaction. Reaction did not proceed when batch reheated.
43-57	0-50% reprocessed oil used in these successful batches. Average particle size of sodium dispersion ranged from 15 to 70 microns, hydriding temp. 235-260°C. Mean hydriding time, 2.1 hrs. 150 lb. Na drum used in some batches.
58	A black batch; discarded. Resulted when this batch was inadvertently added to R-1 reactor which still held Batch 57. Impeller blade damaged; agitator pulled and blade straightened.
59-60	These batches were also dark and discarded. Batch 59 was also inadvertently cooled too much midway in hydriding. Suspect carryover of Batch 59 contamination into Batch 60 despite reactor washout with kerosene and methanol between batches.
61-62	Satisfactory batches, 150 lb. Na drums, all new oil.
63	Hydrogen feed line plugged midway in batch. Reactor cooled, pressure relieved and probe removed for cleaning. Hydrogen pick-up did not resume when batch restarted.
64	Good batch.
65-68	Dark batches, all made with new oil, 135 lb. Na charges.
69-86	All good batches and utilized new oil. No dispersing agent used in most batches; C.P. oleic acid in a few.

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Because hydriding involves the reaction between a gas and a small globule of dispersed liquid, the reaction rate obviously depends upon good contact between the two phases. Some variations in equipment intended to improve this factor were evaluated during the course of these operations. In Batches 1 through 14, the original 6 inch diameter Premier Mill agitator was used. In all succeeding batches, an 8 inch diameter Cowles Dissolver blade, fitted on the agitator shaft in place of the Premier Mill unit, was employed with distinctly superior results. Beginning with Batch 34, the reactor system was further modified by the addition of a high temperature recirculating pump and a liquid distributor plate located on the upper portion of the agitator shaft. All pump packings evaluated in this situation, i.e., circulation of sodium-sodium hydride dispersions at 200°C to 300°C, failed after a very limited life. While the change was considered beneficial, reliability was not sufficiently developed for regular use. However, this facility did prove useful for rinsing out the reactor, a very important element in successful operation.

In addition to gas-liquid contact, the surface condition of the liquid sodium globule was also important. It is believed that this factor distinguished success from failure. Whenever a batch failed to go to completion, the sodium globules were probably coated or otherwise inhibited from reacting. Impure dispersing agent has already been mentioned as a possible inhibitor; breakdown products of the oil when exposed to high temperatures, 300°C or more, is another; reprocessed oil, which always contained trace amounts of solvents and coloring agents, could possibly cause trouble; and sodium hydride contamination from a previous batch seemed unsatisfactory. Because no absolute criterion for these matters existed, care was exercised to keep them under control. Because of this, the following elements of the operating procedure are emphasized:

1. The reactor should be clean before a batch is started. An oil rinse following each batch is recommended to minimize batch to batch contamination. If a black batch has been made, a more thorough washout is necessary. Kerosene, followed by methanol, was used for this purpose. Appropriate consideration was given to the safety factors involved.
2. Batch ingredients must be clean and free of contaminants.
3. Use of dispersing aids such as oleic acid should be held to a minimum and preferably should not be used at all. When reprocessed oil is used in any proportion, no dispersing agent should be added.
4. The nitrogen atmosphere above the liquid should be thoroughly removed and replaced with hydrogen after the sodium dispersion is made and before the temperature is raised for hydriding. This is best accomplished by evacuating to about 24 inches (Hg) vacuum and backfilling with hydrogen two or more times.

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5. Good temperature control during hydriding is essential, the desired range being 250 to 265°C. Excessive temperatures result in carbonization while low temperatures stop the reaction, making restart difficult or impossible.

B. Sodium Borohydride (Step II-A)

Of the 29 batches of sodium borohydride attempted (Table 12) twenty were of good quality (NaBH_4 assay of 88% or better), two were usable (NaBH_4 assay of 78-87%), and six were not used because of low assay. One other batch was not completely processed because of extensive dilution with filter aid (Johns Manville Hi-Flo).

Early batches proved that a good quality sodium hydride slurry is essential to satisfactory sodium borohydride production. Thus, some of the poorer quality hydride batches were discarded without attempting the sodium borohydride operation. The selectivity exercised as the result of this early background information was effective in substantially increasing the consistency of results as shown in Table 12 and Figure 11. Starting with Batch 17, only two batches were processed to completion which assayed less than 85 per cent sodium borohydride; both used sodium hydride of borderline quality. Batch 21 sodium hydride slurry analyzed 1.1 per cent free sodium and made sodium borohydride of only 65 per cent purity. Batch 27 did not contain free sodium but was dark in color. The resulting sodium borohydride batch assayed 78.4 per cent; not high quality, but usable.

The major impurity was found to be sodium tetramethoxyborate, $\text{NaB}(\text{OCH}_3)_4$. A relatively lump-free, off-white powder was evidence of a quality product. Off-quality material was brown to black and somewhat lumpy. Some of the lower quality product tended to be pyrophoric, probably due to the presence of small particles of free sodium. It was quite hazardous to handle, particularly when still contaminated with residual solvent.

The last ten batches produced, excluding Batch 27 mentioned before, averaged 92.4 per cent purity and 83.3 per cent yield (based on sodium charged to the sodium hydride reactor R-1) compared with process design figures of 95 and 83.4 per cent, respectively. The last five batches maintained this same average purity level (92.4%) at a higher average yield, 86.8 per cent. Thus, Step II did achieve design results except for a slightly low product purity.

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TABLE 12

PREPILOT PLANT STEP II-A
Sodium Borohydride Methyl Borate Process

BATCH NO.	TOTAL CYCLE TIME (HRS.) (a)	REACTION TIME (HRS.)	CENTRI-FUGE TIME (HRS.)	R-2 LIQ. TEMP. (°C)	WASH QUANTITY (LBS.)	SOLVENT IN WET CAKE (WT. %)	DRY CAKE WT. (LBS.)	NaBH ₄ IN PRODUCT (WT. %)	YIELD (b) (%)
1	47	3.0	5.7	50	770	-	38.0	93.5	82.5
2	41	1.0	14.0	53	1099	-	58.5	68.0	90.2
3	34	0.4	4.7	57	710	-	30.0	10.0	7.0
4	70	2.4	5.5	48	780	-	45.5	50.0	51.6
5	42	2.0	5.6	38	683	22.7	46.0	84.4	89.2
6	43	1.7	3.1	45	756	-	30.0	89.9	60.9
7				NaH Discarded					
8	62	0.9	33.0	40-55	660	-	49.5	55.0	62.5
9	38	2.7	6.0	50	562	-	34.5	92.0	73.3
10				Na Dispersion Discarded					
11	40	1.1	10.5	60	420	4.9	39.0	89.0	77.7
12	40	2.0	6.2	45	672	Negligible	44.0	92.0	90.7
13				NaH Discarded					
14				NaH Discarded					
15	45	1.3	3.4	55	672	7.0	40.0	95.1	86.5
16	60	0.8	45.0	62	704	14.9	77.5	49.1	86.6
17	66	3.5	7.9	40	567	Negligible	33.0	96.0	80.2
18	47	2.7	4.25	41	798	6.0	39.0	94.6	83.3
19	54	1.7	6.5	48	649	14.0	40.0	88.0	80.9
20	38	1.8	3.7	53	400	2.0	28.0	90.0	57.5
21	55	2.4	25.0	34	747	-	70.0	65	106.2
22	44	3.1	7.3	54	672	7.0	38.0	91	79.0
23	46	2.2	5.25	57	630	3.0	39.0	90	79.4
24	46	1.0	4.4	59	561	3.0	39.0	90	79.7
25	41	2.2	4.5	50	672	4.0	34.5	91	72.5
26	37	2.0	7.5	48	588	10.1	40.0	97	88.2
27	36	2.2	15.5	55	374	2.5	30.0	78	53.6
28	36	1.9	7.5	72	630	Negligible	42.0	92	91.6
29	49	2.0	34.0	58	546	(c)	(c)	(c)	(c)
30	41	2.7	13.0	52	1076	Negligible(d)	39.0	98	87.5
31	36	1.2	10.0	58	609	1.3	39.0	89	80.8
32	32	3.3	9.0	50	504	1.2	41.0	91	85.4
33	30	1.5	6.0	54	608	1.2	42.0	92	88.5

(a) Total cycle time - Start of NaH addition to start of NaH of following run excluding unavoidable delay time. (Step II-A and II-B).

(b) Based on sodium charged to sodium hydride reactor.

(c) Product not processed; contaminated with filter aid.

(d) Continued Batch 2 - from R-2 without filtering. Filtrate - black.

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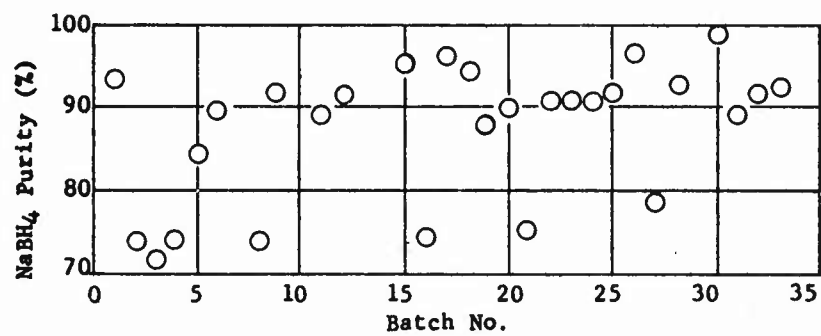


Figure 11. Purity of Sodium Borohydride Batches

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C. Regeneration of Trimethyl Borate Solvent and Oil Recovery (Step II-B)

Solvents and oil were recovered from all batches which proceeded to the borohydride stage. As indicated in Table 13, a total of 29 batches were neutralized with a boron halide; 19 with boron trichloride, 8 with boron trifluoride and 2 with a mixture of these.

Usage of boron trichloride averaged 102.3 per cent of theoretical, but there was some considerable variation from batch to batch. It would normally be expected that due to some losses, somewhat more than the theoretical requirement, would be consumed. This was true for the best quality batches of sodium borohydride, with most of the figures falling in the 100 to 110 per cent range. Consumption for low quality batches was generally more erratic. Where the product contained substantial quantities of $\text{NaB}(\text{OCH}_3)_4$, less neutralizer would be required. On the other hand, if the sodium hydride batch contained free sodium, more neutralizer would be needed.

The average usage of boron trifluoride for eight batches was 149 per cent of theoretical when calculated on the basis of a mole per mole substitution for boron trichloride. This higher consumption of acid reagent was caused by the formation of sodium fluoborate, NaBF_4 .

Salt separation was attempted by centrifuging in the early batches but was unsuccessful due to the extremely fine crystals formed in this organic medium. Several possibilities for improving filterability were evaluated in the laboratory without success. Thus, solvent recovery from these batches involved distilling off tetrahydrofuran and trimethyl borate (THF-TMB) from an oil-solvent-salt mixture in reactor (R-2). As this mixture became depleted in solvent, it approached an oatmeal consistency, interfering with heat transfer and reducing the extent of solvent recovery. Solvent recovery for boron trichloride neutralized batches averaged 84 per cent.

The mixture of NaF and NaBF_4 formed in BF_3 -neutralized batches was readily centrifuged and solvent recovery was increased to an average of 92 per cent of that charged.

Oil recovery and reclamation in batches neutralized with boron trichloride were completed by dissolving the salt from distillation residues and separating oil from the resulting brine prior to purification. Oil purification involved washing and steaming to remove solvents, followed by drying and filtration. Reprocessed oil obtained from treatment of early batches was not satisfactory for reuse in Step I, but about midway in the batch series, a commercial oil purifier (Hilco) was obtained which purified recovered oil to usable limits. Recovery of oil suitable for reuse amounted to 60 and 70 per cent for two batches neutralized with boron trichloride and 90 per cent for a batch neutralized with BF_3 .

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TABLE 13
STEP II-B
(Neutralization Step)

BATCH NO.	SOLVENT REGENERATION TIME (HRS.)	INITIAL NaOCH_3 CONC. (G/L)	ACID REAGENT USED (LBS.)	NA F FILTERED (LBS/WET)	CENTRIFUGE TIME (HRS.)	DISTIL. TIME (HRS.)	SOLVENT LOSS (LBS.)
1	7.4	65.0	BCl_3 120	-	0.2	9.0	340
2	3.5	60.0	BCl_3 151	-	-	8.1	710
3	1.6	28.6	BCl_3 91	131	9.8	6.0	672
4	4.2	59.2	BCl_3 236	100	9.0	12.0	634
5	3.7	49.1	BCl_3 134	-	-	13.0	260
6	12.8	58.6	BCl_3 (a) 193	-	6.5	11.8	336
7	No run						
8	9.5	54.0	BCl_3 (a) 158	-	-	16.8	210
9	4.7	57.2	BCl_3 157	-	-	11.0	630
10	No run						
11	3.0	54.5	BCl_3 139	-	-	11.5	346
12	5.2	57.9	BCl_3 146.5	-	-	13.2	145
13	No runs						
14							
15	7.4	51.1	BCl_3 (b) 204	-	-	14.5	430
16	7.1	45.9	BF_3 107	229	10.7	10.0	210
17	5.0	-	(c)	87 ^(d)	6.5	5.7	147
18	2.5	54.3	BCl_3 136	-	-	14.0	252
19	No run						
20	2.3	41.1	BCl_3 95	-	-	12.0	273
21	4.0	79.0	171 ^(c)	31 ^(e)	10.0	4.5	147
22	5.5	-	BF_3 113	229	10.0	3.5	185
23	4.6	-	BF_3 101	183	9.8	2.0	201
24	2.2	56.5	BCl_3 142	-	-	13.7	210
25	4.3	-	BCl_3 132	-	-	11.7	410
26	4.0	50.4	BCl_3 132	-	-	13.0	260
27	3.0	62.5	BCl_3 142	-	-	13.5	460
28	3.0	59.2	BCl_3 147	-	-	13.0	140
29	4.5	61.4	BF_3 122.5	313	4.5	3.2	240
30	6.0	46.7	BF_3 121.5	265	9.0	5.5	120
31	9.5	50.2	BF_3 115.5	257	5.3	4.0	210
32	4.5	56.0	BF_3 112.5	215	6.9	3.5	280
33	6.0	64.0	BF_3 145.5	279	4.6	4.5	120

(a) Estimated.

(b) Includes substantial but indeterminant amount of material from poor batch.

(c) BF_3 and BCl_3 Mix.

(d) NaF and NaCl filtered poorly, only 37 lbs. cake contained in 6.5 hours. Discovered leaky rupture disc, R-2. May account for some BF_3 usage.

(e) 121 lbs. BF_3 then 50 lbs. BCl_3 used. NaF, NaBF_4 and NaCl mix filtered poorly. Gave up after 10 hours and resorted to distillation

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Conditions promoting good solvent regeneration and recovery were good filtration of borohydride product and freedom of filtrate from same; closed reactor (R-2) system and solvent temperatures within range of 50 to 60°C; moderate rate of acid reagent addition such that side reactions are held to minimum (4-5 hrs. per batch); close check on progress of reaction through weight of acid reagent and analysis of reaction mixture.

Conditions promoting good solvent recovery by distillation were salt free solvent-oil mixture (in case of BF_3 batches); use of agitation; as high an end temperature as could be obtained by steam heated vessel jacket; and nitrogen displacement of solvent vapors in the vessel at the end of distillation.

Conditions promoting good oil recovery and reclamation were efficient washing of the oil to remove salt and solvent; steaming to remove last traces of solvent with care taken to prevent oil loss due to foaming; careful drying and filtration at reduced pressure (24-25 in. Hg.) and at a temperature of 375°F. through filter media containing activated charcoal (Darco G-60) and a commercial Fullers earth (Hilite).

D. Diborane Generation

A summary of the twenty diborane NaBH_4 -Ansul Ether runs is presented in Table 14. It is seen that this process successfully produced diborane of good purity (85% avg.) in better than design yields (87% avg. vs. 67% design). The major impurity was hydrogen, with methyl chloride also present to the extent of about one mole per cent. The operation was reliable and the equipment generally performed well. Particularly noteworthy was the horizontal screw reactor (R-3) which did not plug at all in contrast to AFN's previous experience with a reactor lacking agitation. The Lapp Pulsafeeder used to meter feed solution to the reactor was somewhat troublesome, but close attention, coupled with quickly learned operating tricks such as a momentary speed-up to clear the pump, minimized the problem.

Mechanical problems prevented the diborane absorber from being completely successful. Although the absorber column (C-2) was glass, it soon became coated by dark feed solution so that column action could not be observed. The high capacity of the recirculating pump (P-6) caused the column to flood, and the solution to plug the gas outlet and sampling lines. In addition, the gas inlet line was located in a position where solution could splash into it, and it plugged also. Lastly, the performance of the recirculating pump, a Chempump, was erratic. It tended to overheat and kick out its thermal switch, so water was usually trickled over the pump housing for cooling; moreover, its output was not consistent, probably due to an NPSH problem. These problems, although not completely eliminated, were minimized through minor piping rearrangements and careful attention to the trouble spots.

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TABLE 14
Diborane Generation Summary, NaBH_4 -Ansul Ether Method

Run No.	NaBH_4				BCl_3 (lbs.)	Conv. (a) (%)	B_2H_6		
	Source	Gross (lbs.)	Purity (wt. %)	Net (lbs.)			Avg. Purity (mole %)	Net (lbs.)	Yield (b) (%)
1	Metal Hydrides	36.9	98.0	35.3	53.0	100	-	-	-
2	AFN-1	38.0	93.5	35.2	33.5	100	-	-	-
3	AFN 5 & 6	44.0	91 & 71	37.0	9.5	53	-	-	-
4	AFN 5 & 2A	55.0	84 & 69	42.8	29.5	100	-	-	-
5	AFN-9	34.5	92.0	32.1	33.5	100	-	-	-
6	AFN-11	39.0	89.0	34.7	35.0	100	95	16.2	97
7	AFN-12	44.0	92.1	40.5	33.5	87	80	13.5	79
8	AFN-15	40.0	95.1	38.0	30.5	100	85	5.1 (c)	-
9	AFN-17	33.0	96.0	31.7	27.8	74	73	13.6	115
10	AFN-18	39.0	94.6	36.9	31.0	87	90	16.9	109
11	AFN-19	40.0	88.0	35.2	34.6	59	84	11.7	98
12	AFN-20 and Metal Hydrides	36.0	90 & 98	33.2	32.0	92	88	7.2	71
13	AFN-22	38.0	91.0	34.5	35.0	81	84	13.1	-
14	AFN-23	39.0	90.5	35.3	39.0	100	97	13.9	81
15	AFN-25	34.5	91.2	31.5	39.5	100	86	15.2	99
16	AFN-26	40.0	96.9	38.7	41.5	100	90	16.9	90
17	AFN-24	39.0	90.2	35.2	32.0	90	-	12.6	79
18	AFN-28	42.0	92.5	38.9	33.0	86	90	12.0	86
19	AFN-31	38.0	89.3	33.9	32.5	89	78	12.2	76
20	AFN-30	39.0	98.6	38.5	30.5	100	67	10.8	70
					Average		85		87

(a) Based on NaBH_4 in final apent.

(b) Based on NaBH_4 .

(c) Abortive run.

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Filtration of the spent solutions to remove sodium chloride was slow but satisfactory. Usually 5 to 10 pounds of filter aid were added to the centrifuge to speed the operation. Sometimes the cake was pyrophoric, apparently because of unconverted sodium or sodium hydride. A typical set of analyses for this operation is compared with design figures in Table 15.

TABLE 15

Spent Solutions - Diborane Generation NaBH₄-Ansul Ether Method

	Unfiltered Spent			Filtered Spent			Salt Cake			
	NaCl (Wt.%)	NaBH ₄ (Wt.%)	B (Wt.%)	NaCl (Wt.%)	NaBH ₄ (Wt.%)	B (Wt.%)	Wt. (lbs.)	NaCl (Wt.%)	NaBH ₄ (Wt.%)	B (Wt.%)
Run No. 4 (typical)	12.0	-0.14 ^(a)	1.90	0.60	1.89	2.57	76.1 ^(b)	67.1	1.99	4.39
Design	11.8	0.00	0.00	0.00	0.00	0.00	57.0	94.0	0.00	0.00

(a) Spent was slightly acid.

(b) Includes 6 lbs. filter aid. Cake was pyrophoric.

In theory, the spent solution should contain nothing but Ansul Ether 181 and salt, but it was apparent from the analyses that the actual situation was more complicated. These solutions were generally quite active with water and continued to release gases on standing. They had a characteristic odor different from diborane. For control purposes, chloride was reported as NaCl and alkalinity as NaBH₄. Total boron was determined by the standard mannitol-boric acid titration. While adequate for guiding the pilot plant operations, these reported analyses brought up inconsistencies which could not be explained in terms of simple chemistry. The most significant conclusion is that the solutions and solids contained boron values that could not be converted to diborane through the addition of boron trichloride.

Data for Runs 21 through 40, which used the modified process of diborane generation, are presented in Table 16. This process again proved successful by providing an adequate and reliable supply of diborane for pyrolysis studies. Also, it offered certain advantages over the sodium borohydride-Ansul Ether process while maintaining equal or better yields and gas purity: (1) the extra operations of isolating and drying sodium borohydride, as well as subsequent solutioning in Ansul Ether, were eliminated; (2) the solvent system employed was more economical; and (3) the salt formed was more readily filtered.

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TABLE 16

Diborane Generation Summary
Modified Process, Runs 21-40

Run No.	Reactor Used	Feed Batch No.	BCl ₃ ^(a) (lbs.)	B ₂ H ₆			
				Wt. (lbs.)	Avg. Pur. (mole %)	Equil. Pur. (mole %)	Yield ^(b) (%)
21	T-7	34	108	7.8	92	97	65
22	T-7	34	91	8.2	90	97	86
23	R-3	34	109	10.0	91	97	62
24	T-7	34	100	13.5	96	100	113
25	T-7	35	89	7.3	80	92	69
26	T-7	35	89	Chromatograph inoperative			
27	T-7	35	90	7.5	88	94	71
28	T-7	35	88	5.5	87	95	54
29	T-7	35 & 36	91	7.6	90	96	70
30	T-7	36	84	6.9	92	97	69
31	T-7	36	94	(c)	-	85	-
32	T-7	36	73	7.3	94	96	85
33	T-7	36	81	5.8	93	94	68
34	T-7	37	90	7.5	88	88	70
35	T-7	37	(d)	-	-	-	-
36	T-7	37	92	10.5	89	92	97
37	T-7	37	88	5.9	87	92	63
38	T-7	37	88	5.1	79	85	49
39	T-7	38	88	8.5	89	100	84
40	T-7	38	93	8.6	97	100	78
Avg.					89.5		74

- (a) Includes proportionate share of BCl₃ used in R-2 to make feed slurry.
(b) Based on BCl₃ converted.
(c) Run interrupted for 3 days. Purity low on restart and gas vented.
(d) T-7 not completely emptied from previous run due to gauging difficulties. Diborane purity low and gas vented.

Although the indicated yield of 74 per cent was lower than the 87 per cent reported for the sodium borohydride-Ansul Ether method, the latter figure does not include the Step II yield of 83 per cent for producing sodium borohydride. Thus, the combined yield for the two steps was 72 per cent and is to be compared with the first figure above.

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The sometimes gelatinous and gassy character of the feed slurry introduced problems not fully appreciated from the laboratory studies. It was found that the Milton Roy metering pump (P-41) could not reliably handle this material. Much effort was expended toward its successful use, but pumping difficulties continued. Consequently, the "tank method" of diborane generation was utilized.

In this method, a charge of feed slurry from the sodium borohydride reactor (R-2) was pumped into the spent solution tank (T-7). Continuous agitation was provided by both the agitator in the vessel and by recirculation with the new Peerless Pump (P-61). The tank was externally traced with copper tubing which could provide either cooling or heating with steam. With cooling water circulating through the tracing, boron trichloride was metered into the vapor space above the slurry. Diborane was thus generated at a uniform rate and fed to the pyrolysis unit. Boron trichloride addition was stopped when the slurry became neutral, at which time the tracing was changed to a heating cycle, driving off residual diborane dissolved in the slurry.

Even with the tank method of diborane generation, high viscosity slurries caused operating difficulties. First, the agitator in T-7 was not sturdy enough and tended to whip. This action caused the mechanical seal to leak and eventually bent the agitator shaft. A heavier duty agitator was installed and was satisfactory. Secondly, the slurry sometimes did not flow sufficiently well to keep the suction of the circulating pump (P-61) flooded. This condition was remedied by enlarging and changing the configuration of the pump suction line. Finally, level indication in the generating tank T-7 was not reliable despite the installation of an electronic level indicator (Robertshaw-Fulton Level-Tel). An overflow system was eventually determined as suitable. Despite these mechanical difficulties, the over-all results were generally satisfactory.

Filtration of the spent slurry was satisfactory. In contrast to the earlier process, no filter aid was used. The change in process did not eliminate the occasional batches of pyrophoric cakes. Cakes averaged about 50 per cent solids.

As the prepilot plant program continued, the pyrolysis and alkylation steps were emphasized while the steps through diborane generation received minimum attention. Thus, extensive calculations and material balances were not completed for Runs 41 and beyond. Essential information as to quantity and purity of the diborane produced is included in the pyrolysis data for those runs (Volume IV).

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II. Operating Procedures

A. Preparation of Sodium Dispersion

Metallic sodium (melting point 98°C) was received in metal drums containing approximately 106, 135 or 150 pounds of bulk metal. One drum was attached to reactor (R-1) through a double valve coupling assembly and the contents were heated to approximately 120°C by two band heaters (upper and lower). Simultaneously, the sodium inlet line to R-1 and the valve assembly were heated by a "Calrod" tube heater.

An oil charge, weighing three times the net content of the sodium drum, was placed in R-1 from the metering tank (T-1). The mineral oil was heated to a temperature of 130°C and oleic acid dispersing agent (0-1000 ml.) added.* The agitator (A-1) was started at high speed and R-1 was placed on the balanced vent system under a nitrogen atmosphere.

Sodium addition was started at such a rate that the contents of the drum were added within a period of 0.3 to 0.8 hour. Liquid sodium in the drum was displaced by nitrogen. A free flow of nitrogen through the drum and valve assembly was one evidence of completed addition. After the metal addition, valves were closed on the sodium drum and line, and the heating elements (band and tube) were switched off.

Agitation of the oil-sodium mixture was continued at 130°C for a period of about 0.5 hour. Samples were taken for particle size which was determined by use of a microscope equipped with a graduated eyepiece. A dispersion having an average particle size of 50 microns or less was considered satisfactory for preparation of sodium hydride.

B. Preparation of Sodium Hydride

Reactor (R-1) containing the sodium dispersion was sealed and the system evacuated to 24 in. Hg. and backfilled with hydrogen. Evacuation and backfilling were repeated to further reduce nitrogen content of R-1.

Hydrogen was supplied from 12 cylinder banks arranged so that one half of the bank, or six cylinders, could be used independently of the other six. The contents of six cylinders were more than enough for one standard batch of sodium hydride. Cylinder pressure of 2200 to 2400 psig was reduced to 50 psig by a regulator and the gas flow directed a flow indicator and check valve into R-1 by means of a sparging tube.

*Where recovered oil (reprocessed) was used, no dispersing agent was required.

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The temperature of R-1 was increased from 250°C to 260°C and consumption of hydrogen increased with increase in temperature commencing at 170°C to 180°C. Because the reaction forming sodium hydride is exothermic, it was necessary to put the Aroclor circulating system on a cooling cycle to prevent overheating (i.e., over 300°C). Hydrogen usage could be followed on the flow indicator but a more reliable index was the decrease in cylinder pressure as presented on the hydrogen regulator pressure gauge. Hydrogen addition was complete within two or three hours and the reaction mixture cooled to a temperature of less than 150°C before sampling.

The sodium hydride-oil mixture was sampled for appearance and analyzed for free sodium content. A good hydride batch has a consistency slightly heavier than pure oil and a blue-gray to milky white appearance. Free sodium was determined by use of a high frequency device and a content of 0.5 per cent or less was acceptable.

The completed sodium hydride batch was then cooled to about 110°C under residual hydrogen pressure (20-30 psig) in preparation for the next step.

C. Preparation of Sodium Borohydride (Methyl Borate Process)

A mixture of two solvents, tetrahydrofuran (THF) and trimethyl borate (TMB) was prepared on an equiweight basis and stored in tanks (T-3) and (T-4). A total of 2320 pounds of mixed solvent was charged to Reactor (R-2) and then heated to 50°C with agitation. R-2 was placed on the balanced vent system and a batch of sodium hydride in oil was pumped in via (P-1) so that the addition did not take less than one hour and R-2 temperature did not exceed 60°C. When addition was complete, R-1 was washed with oil from T-1 (50-100 lbs.) and the washings transferred to R-2.

The prepared sodium borohydride slurry in R-2 was maintained at a temperature of 50°C and solids removed by use of the perforate basket centrifugal filter (K-3). The basket was lined with either paper or cloth as a filter medium.

The sodium borohydride cake was washed with fresh mixed solvent (500-700 lbs.),* spun dry, and removed from the filter. Wash solvent filtrate was collected in tank T-22 and transferred to the fresh solvent storage tank (T-3 or T-4).**

*The quality of product is directly related to the quantity of wash solvent used.

**Tanks T-3 and T-4 were used alternately to supply the batch charge to R-2. The tank supplying the charge held the fresh wash from the previous batch and received the filtrate from the sodium borohydride slurry.

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Sodium borohydride filter cakes, two per normal batch, were removed from the filter as a wet cake, protected by a nitrogen filled plastic bag, and weighed. The wet cake was then spread on trays and dried in a vacuum oven (D-1) at about 84°C and a vacuum of 24 inches (Hg.) for at least four hours. After cooling, the dried cake was removed from the oven, weighed, sampled and stored in sealed metal drums with a plastic bag liner.

The filtrate from the borohydride slurry was collected in Tank (T-22) and then transferred to the batch charge tank (T-3 or T-4) for regeneration in the next operation.

D. Regeneration of Trimethyl Borate

The filtrate from the sodium borohydride slurry, stored in either Tank T-3 or T-4, was returned to reactor (R-2) and heated to 50°C with agitation.

The reactor (R-2) was removed from the balanced vent system and placed on a closed system with the vapor condensing facilities set for total reflux.

A sample of the liquor was taken from the recycle line and analyzed for NaOCH_3 content by titration of an aliquot portion with standard acid solution, using methyl red as an indicator. This determination, also obtained by use of a high frequency device with sensing element located on the liquor recycle line, was used to follow the reaction.

The acid reagent was weighed and conducted into R-2 through a manifold system which contained a pressure regulator (set to maintain a maximum of 15 psig), flow indicator, and check valve. Either boron trichloride or boron trifluoride was used, supplied from cylinders containing 100 and 60 pounds of reagent, respectively. Boron trichloride cylinders had a normal pressure of 20 to 30 psig, and were heated by use of band elements to maintain pressure under flow conditions.

E. Diborane Generation

1. Sodium Borohydride-Ansul Ether Process

a. Solution Preparation

Filtered spent solution was transferred from the filtrate receiver (T-19) to the feed solution preparation tank (T-5) by means of a transfer pump (P-5). Both these tanks, as well as others in the system, were under a 3 to 5 psig nitrogen blanket. A level gauge on T-5 was used to determine when the proper amount of solution, usually 390 pounds, had been added. Any make-up Ansul Ether 181 required was added directly to the tank from a drum by an air-operated drum pump.

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A batch of sodium borohydride from Step II was added by hand to the hopper above tank T-5 after weighing. The ratio of NaBH_4 to Ansul Ether was adjusted to result in a nine per cent solution, approximately. The hopper was then evacuated and backfilled with nitrogen to a pressure of 35 psig. The Jamesbury ball valve between the hopper and tank was opened and the powdered sodium borohydride blown into the tank. The agitator was turned on.

The solution of sodium borohydride in Ansul Ether 181 is exothermic. Without cooling, the temperature of the solution will rise to 60 to 70°C. After some four hours, the heat evolution was no longer evident and the borohydride was considered dissolved.

Solutions made from sodium borohydride of less than 90 per cent purity were filtered in K-3 after several pounds of Celite filter aid were added. When greater than 90 per cent purity sodium borohydride was used, the solutions were run through a cartridge filter at the absorber inlet.

The batch of dissolved sodium borohydride was then transferred to the absorber tank (T-9) by means of pump (P-5). Here the solution was recirculated through the absorber column (C-2) during the course of a pyrolysis run where it contacted the off-gases from the pyrolysis unit, picking up the unused diborane and forming the adduct $\text{NaBH}_4 \cdot \text{BH}_3$. After this enrichment step, the batch of feed solution was transferred to the feed solution storage tank (T-6) for metering to the diborane generator.

Although feed solutions were prepared and handled in batches, the above steps could be carried out in a manner which always kept some feed solution in tank T-6. Thus, diborane generation could be carried out continuously.

b. Generation

Sodium borohydride solution and boron trichloride were metered into one end of the diborane generator (R-3) in stoichiometric proportions. The Lapp Pulsafeeder (P-4) maintained a constant solution flow rate which was checked with a flowmeter and also by periodically pumping into a calibrated volume tube. The solution rate was carefully watched because the metering pump sometimes faltered. The major sources of trouble in this respect were (1) a gassy feed solution causing gas pockets in the pump or suction line and (2) inoperative pump check valves caused by binding or solids.

Boron trichloride was fed from a single gas cylinder heated by an electric band heater. During the summer, this heater was over-powered

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and required continued attention. With ambient temperature of 60°F. to 90°F., this heater could be operated almost continually when feeding at the normal rate. The boron trichloride was metered at 15 psig in order to have a sufficient pressure available at the generator. It was necessary to steam trace and lag the entire feed system to prevent boron trichloride from condensing in the rotameter and lines. The indicated gas temperature was 40°C downstream of the rotameter.

The boron trichloride feed rate was established initially from knowledge of the feed solution composition and flow rate. Minor adjustments were made during the run depending on the analysis of the spent solution exiting from the reactor, i.e., whether it was acid or alkaline in water solution. In general, spent solution was kept slightly alkaline since an acid spent solution would generate diborane in contact with sodium borohydride during preparation of the subsequent feed batch in tank T-5. Approximately one hour elapsed before a change in feed rate to the reactor would be fully reflected in the composition of the spent solution.

Because the reaction to form diborane is exothermic, cooling water flow was maintained through the first two of the three jacket sections on the diborane generator, R-3. The moderate temperature minimized side reactions, including breakdown of the Ansul Ether. The reactor screw revolved at approximately one rpm and effectively prevented reactor plugging. The reactor in the decaborane unit previously operated by AFN, Inc. had no internal screw, and plugging had been a recurring problem.

Diborane left the opposite end of the reactor from the feed. Before being sampled and metered to the pyrolysis section, the diborane passed through a cold trap (E-2) maintained at -40°F. to -80°F. with dry ice. The cold trap collected about eight ounces of liquid during a 24 hour period of operation. This liquid was evacuated down the wet vacuum pump. The combined volume of R-3 and the spent solution of receiver T-7, both initially filled with nitrogen, was large in relation to the diborane generation rate. Because of this, diborane purity was low for several hours at the start of a run. High purity diborane was obtained more quickly by starting the run with the diborane generating section under a vacuum. Since an influx of air could result in an internal explosion, the system was always thoroughly checked for tightness before feeding the reactants to the generator.

c. Spent Solution Filtration

The spent solution was filtered in the Tolhurst 20 inch centrifuge using paper (Rochester Paper Co. Code 1171). Cotton canvas was used in some runs but it became embrittled and was difficult to use. Several pounds of Celite 505 or Hi-Flo Super Cel filter aid were placed

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in the bowl prior to the filtration. Often some filter aid was added to the spent liquor as well. The centrifuge bowl had to be emptied before the filtration was complete because of the large amount of salt cake. This intermediate cleaning resulted in some lost time since it was necessary to evacuate the centrifuge before opening it.

A more practical procedure for filtration was to pump all the spent solution through K-3, neglecting any overflow over the basket. The solids were then removed and the filtrate cleaned by recirculation. Four to six hours were generally necessary to complete the filtration. However, 60 to 70 per cent of the salt could be removed in the first pass which could be completed in 10 to 15 minutes.

The salt cake was a rather solid mass similar in consistency to wet clay and ten minutes or more were required to remove this cake. Often the cakes were pyrophoric but the fires were smothered by closing K-3 and introducing nitrogen. No correlation was obtained between the length of time taken to evacuate K-3 and the tendency of the salt cake to become pyrophoric. K-3 was evacuated for 20 minutes to as much as several hours prior to being opened.

2. Modified Process

a. Feed Slurry Preparation

A heel from the previous batch of feed solution was left in the Step II Reactor (R-2). The quantity of heel was not important if the minimum of about 100 pounds was exceeded. Since R-2 was not equipped with a level indicator, the volume of heel had to be estimated, a difficult task in this round bottom, completely enclosed vessel. Usually the vessel was stick-gauged, but even this was not accurate because of the round bottom. Moreover, opening the vessel consumed time in bolt removal and replacement around the sight glass, and in eliminating any air that might have entered.

Recycle filtered spent from Step III was added to R-2 from storage tank T-4 after analysis for diglyme (Ansul Ether 141). Usually two batches of sodium hydride with their oil rinses were pumped over from Step I. Make-up mineral oil and diglyme were then added to bring the charge, exclusive of heel, into the following ratio: 82 mineral oil, 9 diglyme, 9 sodium hydride.

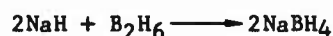
Boron trichloride and boron trifluoride were then simultaneously metered into the vapor space of R-2. At first, electric band heaters were used to vaporize boron trichloride from 10 pound (wt.) cylinders placed on weigh scales. Eventually a steam-jacketed metering tank was installed. This was filled intermittently from a one ton (nominal) cylinder. Three-fourths of the total acid reagent required

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to neutralize the sodium hydride was added at this point with boron trifluoride making up 2 to 5 per cent of this amount. Cooling water on the jacket of R-2 along with an external, refrigerated exchanger removed the heat of reaction and maintained the reactor temperature at 30 to 35°C.

As in the initial process, feed solution was utilized in tank T-9 and absorber column C-2 to remove residual diborane from pyrolysis off-gases. In the modified process, however, the material used was the diluted sodium hydride slurry before BCl_3 addition. Thus, the chemical reaction involved was:



b. Generation

The prepilot plant was equipped to generate diborane in much the same way as previously, i.e., by metering both feed solution and boron trichloride in stoichiometric proportions to R-3. However, operating difficulties led to the discontinuance of this system in preference to the "tank method". These difficulties centered around the new Milton Roy metering pump installed to move the feed slurry from tank T-5 into the reactor (R-3). (The Lapp Pulsafeeder, used previously, lacked capacity for this method because the sodium borohydride concentration in the feed slurry was about one-third that of the previous method.) Performance of the pump was extremely erratic and unreliable, again because of the gassy nature of the feed slurry and the problem of solids affecting check valve operation. Also the slurry tended to be gelatinous and sometimes did not flow smoothly enough to flood the pump section.

In the tank method, a charge of feed slurry amounting to about one-third of an R-2 batch was put in tank T-7. Boron trichloride was metered directly into the vapor space of the tank. Cooling coils were added to the outside of the tank to remove the heat of reaction. The solids were kept in suspension by the agitator and by external recirculation (pump P-51). The rate of boron trichloride addition was adjusted to give the desired rate of diborane generation and was continued until the slurry in T-7 was neutral. At that time the coils on the outside of the tank were changed to a heating cycle to drive off dissolved diborane. Final slurry temperatures of 50 to 70°C were obtained.

Other aspects of the diborane generation were the same as previously with the diborane passing through cold trap E-2 before being sampled and metered. A wet test meter using mineral oil as the seal fluid was installed in the diborane line to provide better material balance information.

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c. Spent Solution Filtration

Following completion of a diborane generation run, the spent solution was filtered in centrifuge K-3. This was similar to the method used previously except that all the salt produced in R-2 and in diborane generation was filtered at this time. Hence the centrifuge was normally emptied four times. Since there was no longer any THF or TMB in the system, tanks T-19 and T-22 could be used interchangeably. One was generally used as a hold tank for slurry to be centrifuged and the other as the filtrate receiver. Thus it was possible to empty tank T-7, recharge it with a new batch from R-2, and resume diborane generation with a minimum of lost time.

After filtration, oil could be recovered for reuse in Step I as in the past by steaming, drying and filtering.

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SECTION TWO

HYDROGENATION OF BORON TRICHLORIDE

BACKGROUND INFORMATION

The obvious economic advantages offered by a more direct diborane process eliminating use of an active metal spurred AFN, Inc. in early 1958 to investigate the reduction of boron trichloride with hydrogen. A series of experiments conducted in the laboratories of National Distillers and Chemical Corporation at Cincinnati, Ohio demonstrated the feasibility of such a process, described by the following reactions:



In a typical experiment, hydrogen and boron trichloride were pre-mixed in the gaseous state at atmospheric pressure in a mole ratio of 14 hydrogen to 1 boron trichloride and then passed through a glass reactor at 620°C (1148°F.) containing silver metal granules. Residence time of the gases was 0.2 second. Based on a feed stream containing 1 mole of BCl_3 and 14 moles of H_2 , the reactor effluent had the following composition:

BHCl_2	-	0.450 moles
HCl	-	0.474 moles
BCl_3	-	0.542 moles
H_2	-	<u>13.534</u> moles
		15.000 moles

The gas mixture was cooled and passed through a separation system which utilized activated carbon and β, β' dichloroethyl ether. HCl was recovered quantitatively. The mixture of BHCl_2 and BCl_3 recovered from the separation system was refluxed to disproportionate the BHCl_2 and yielded 0.075 mole of B_2H_6 . Based on the data thus obtained, the conversion of BCl_3 to BHCl_2 was 45 per cent, and the yield of B_2H_6 , based on BCl_3 consumed, was 95 per cent.

These excellent results provided the basis for an extension of the existing contract, AF 33(600)-35745 involving a more complete study and scale-up of this process. Eventually a 50 pound per day pilot plant was designed, built and operated at American Potash & Chemical Corporation's Henderson, Nevada facility.

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The combined efforts of AFN, Inc.'s three partners in implementing this program are reported here. Specifically, National Distillers and Chemical Corporation continued the laboratory development, FMC Corporation investigated the process on the prepilot plant scale, and American Potash & Chemical Corporation carried out the pilot plant operations.

SUMMARY

Laboratory Development

The effects of important parameters on the hydrogenation of boron trichloride were determined in the laboratory as follows:

Catalyst	- Silver screens reduced required reactor residence time by a factor of about 7 and were unaffected by reaction conditions. Other catalysts tested, copper, carbon, palladium on carbon, and platinum on carbon, were less effective and reduced yields.
Residence Time	- Catalyst and other reaction conditions determined optimum time.
Temperature	- Conversion of BCl_3 increased with increased temperature, but very high temperatures caused elemental boron formation. Optimum was 700°C .
Pressure	- Increased pressure increased reaction rate and reduced necessary residence time.
Ratio of Reactants	- Conversion of boron trichloride increased with increased H_2 concentration. At 700°C , BCl_3 conversion was 39% when $\text{H}_2:\text{BCl}_3$ mole ratio was 14; about 20% when ratio was 3.

These results must be coupled with engineering and economic factors for the determination of optimum reactor conditions.

Absorption in liquid BCl_3 was found to be the most feasible method for separating the reaction products. Other methods examined and determined to be potentially suitable but less attractive were (1) absorption by complexing with diphenyl sulfide, (2) adsorption on carbon, (3) gaseous diffusion, and (4) absorption in hexane.

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Disproportionation of dichloroborane to form B_2H_6 was accomplished rapidly and quantitatively through the use of a distillation column charged with a mixture of boron trichloride and dichloroborane.

Both the hydrogenation and disproportionation reactions are reversible. Rate constants for the back reactions were determined and other factors were evaluated to guide the process design. Physical and chemical data pertinent to design were accumulated.

Prepilot Plant Evaluation

Prepilot plant investigations, carried on concurrently with the laboratory development program, demonstrated that silver catalyzed hydrogenations reached chemical equilibrium within 0.13 second residence time at 1300°F. (704°C) and 80 to 100 psig pressure. The silver catalyst was unaffected by the net four and one-half days it was operated in an integrated prepilot plant and therefore has a life far in excess of this period.

Of various materials of construction tested, which included carbon steel, Type 347 stainless steel, nickel and monel, only silver-lined (not plated) equipment had adequate corrosion resistance for use as the boron trichloride preheater, reactor and aftercooler. Introduction of hydrogen before the boron trichloride was heated appreciably was also necessary for good corrosion resistance of the preheater. In addition, highly purified boron trichloride was found to be important in avoiding chemical attack of the silver catalyst.

Operation of the integrated prepilot plant incorporating the three principal process steps (hydrogenation, separation and disproportionation) was uniform, reproducible, and predictable. No real loss in yield of B_2H_6 was detected and no evidence was found that any undesired products were formed.

Two problems which arose in evaluating performance were (1) showing that HCl was stripped from the $BHCl_2$ and BCl_3 in the absorber and (2) finding the cause of an apparent B_2H_6 loss. The runs in which HCl was not properly stripped were finally shown to have had little if any flow of stripping H_2 , because of plugging of the small orifice which regulated its flow. The apparent loss in B_2H_6 was shown to have been due to condensation and trapping of liquid B_2H_6 or liquid B_2H_6 -HCl mixtures in the condenser of the disproportionator.

Adequate information was obtained to guide the design and operation of the pilot plant.

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Pilot Plant Design

Laboratory and prepilot plant data were used to design a fifty pound per day diborane pilot plant at American Potash & Chemical Corporation's Henderson, Nevada facility. The unit closely resembles a petroleum refinery in operation and appearance since most of the processing is carried out in distillation and absorption columns.

Common materials of construction and standard models of pumps, compressors and other equipment were utilized. However, the catalytic hydrogenation reactor and its related heat exchanger were silver lined. Design temperatures ranged from 1300°F. (reactor) to -100°F. (diborane condenser); pressures were moderate, 300 psig or less. A unique system was designed to provide the three levels of refrigeration required (-20°F., -50°F. and -100°F.). Safety of operating personnel was provided through the use of outdoor construction, the observance of established standards and codes, the provision of special venting, inerting, and waste destruction facilities, and other protective measures.

Commercially available grades of boron trichloride and hydrogen were to be used as raw materials, although a boron trichloride distillation column was installed for purification of a supply of Air Force boron trichloride having a high phosgene content.

Pilot Plant Operation

Following an initial period of training, equipment cleaning and testing, sixteen runs were made in the diborane pilot plant. The unit performed essentially as designed except for one process problem; the absorbers had insufficient capacity to make a complete separation of hydrogen chloride and dichloroborane at design flow rates. However, a diborane product of 99 per cent purity was obtained by reducing reactor feed rates to 60 per cent of design.

The catalytic hydrogenation reactor operated for a total of more than 1300 hours without indication of a decrease in silver catalyst activity or of a corrosion problem. The design conversion, 20 per cent, of boron trichloride to dichloroborane was demonstrated at design flow rates. The silver-lined reactor effluent cooler was effective in quickly quenching the reaction products and thereby preventing back reaction to detract from the reactor performance.

Changing the packing in the absorbers to a small size was not successful in improving the efficiency of the HCl-BHCl_2 separation because of flooding problems. Best results were obtained by insuring a cold absorbent to the secondary absorber, carefully controlling the operation of the hydrogen chloride fractionator to eliminate hydrogen chloride from the absorbent, and heating the stripping gas to the primary absorber. The

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analytical problems involved in assaying small quantities of hydrogen chloride in a stream containing boron trichloride prevented the determination of which column fell short of design expectations. Nevertheless, it was concluded that the desired separation could be made by longer columns.

No back reaction took place in the absorption columns, but some did occur in the hotter distillation columns. This was effective in improving the purity of the product diborane and by-product hydrogen chloride. The disproportionation and fractionation columns satisfactorily performed their functions.

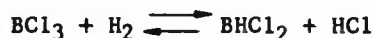
Because none of the pilot plant equipment was spared, mechanical problems sometimes interfered with smooth operations and reduced product yields and purities. Several improvements in mechanical equipment were made during the course of operations, and the knowledge gained would be important in the specification and selection of equipment for a larger plant. This, coupled with the proper sparing of critical equipment items, could be expected to result in reliable over-all plant performance.

The pilot plant production of both diborane and anhydrous hydrogen chloride in purities of 99 per cent and yields, based on BCl_3 consumed, of 95 per cent suitably demonstrated AFN, Inc.'s diborane process. The data and experience gained were adequate to permit the design of a larger scale plant with the confidence of attaining continuity of operation with improved purities and yields.

LABORATORY DEVELOPMENT

I. Process Description

Boron trichloride and hydrogen react in the gas phase at elevated temperatures to produce dichloroborane in accordance with the following equation:



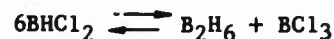
This reaction is reversible and the composition reached at equilibrium depends upon reactor conditions. The free energy change in this reaction is such that conversion to BHCl_2 increases with rising temperature. At ambient temperature, the equilibrium is displaced almost completely to the left, and isolation of product depends on the fact that the back reaction proceeds extremely slowly at ordinary temperatures.

Since the dichloroborane is obtained in admixture with hydrogen, boron trichloride and hydrogen chloride, an essential element of the process is the means of separating it from the other constituents. Furthermore, each of the other components must also be recovered efficiently and in pure form for recycle to the reactor.

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The dichloroborane can be disproportionated to diborane and boron trichloride, according to the equation:



This reaction is also reversible and can be driven all the way to the right only if one of the components is continually withdrawn. This is accomplished by taking advantage of the much greater volatility of diborane over that of boron trichloride.

In the development of these process steps, the following are of major importance:

- Development of a catalyst of maximum activity and life.
- Determination of the optimum reaction parameters.
- Obtaining optimum yields and conversions.
- Separation of dichloroborane from the reaction mixture.
- Obtaining maximum yield in the disproportionation.
- Separation and purification of diborane product.

II. Hydrogenation of Boron Trichloride

A. Effect of Variables

The most important variables affecting the percentage of boron trichloride which is converted to dichloroborane are temperature and the mole ratio, H_2/BCl_3 . Pressure was also found to exert an influence on the conversion. The rate of reaction was found to be increased greatly by the use of certain catalysts and, as would be expected, by pressure.

The yields have been found to depend chiefly on temperature, residence time and type of catalyst. The determination of yield depends on measurement of the amount of BHCl_2 formed compared to the loss of BCl_3 .

1. Temperature

Initial experiments (Table 17) indicated that the conversion of BCl_3 to BHCl_2 increased with rising temperature in the range of 600 to 700°C. This effect is shown in Figure 12. It was also noted that a longer residence time at 700°C resulted in a lowered conversion.

Since the longer residence time was achieved by reducing reactor thruput, it was felt that the slower cooling at the reactor exit which accompanied the reduced flow rate probably permitted the reaction to shift back to the left (back reaction). Therefore, further reactions were conducted in a new quartz reactor in which the reactor tube converges to a small bore immediately after the hot reaction zone.

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TABLE 17

Hydrogen-Boron Trichloride Reaction Data

Expt. No.	Temp. (°C)	Press. (atm.)	Residence Time (sec.)	Mole Ratio (H ₂ /BCl ₃)	Conv. to BHCl ₂ (%)	Catalyst
<u>498-</u>						
66	596	1	0.08	14.0	20.5	Silver, granular
68	610	1	0.08	14.2	16.6	Silver, granular
70	636	1	0.07	13.9	11.8	Silver, granular
74	655	1	0.14	14.9	21.1	Silver, granular
72	652	1	0.15	28.2	22.6	Silver, granular
78	620	1	0.20	15.5	11.0	Silver screen
81	620	1	0.51	15.4	23.8	Silver screen
89	620	1	0.52	14.8	26.2	Silver screen
83	620	1	0.81	14.4	25.2	Silver screen
85	700	1	0.21	14.3	34.7	Silver screen
87	700	1	0.50	15.7	39.0	Silver screen
91	700	1	0.82	13.2	35.0	Silver screen
93	700	1	0.20	7.0	22.7	Silver screen
95	700	1	0.50	8.1	29.0	Silver screen
97	700	1	0.79	8.3	29.6	Silver screen
101	700	1	0.53	4.0	19.0	Silver screen
103	700	1	0.79	3.7	20.0	Silver screen
99	700	1	0.26	34.8	50.3	Silver screen
<u>266-</u>						
268	620	10.2	0.10	14.0	19.2	Silver, granular
269	620	10.2	0.20	14.0	20.6	Silver, granular
271	700	10.2	0.10	14.0	25.8	Silver, granular
270	700	10.2	0.20	14.0	22.8	Silver, granular
272	750	10.2	0.08	14.0	28.8	Silver, granular
259	750	10.2	0.20	14.0	25.5	None
256	750	10.2	0.29	14.0	28.5	None
260	750	10.2	0.55	14.0	23.1	None
263	750	10.2	0.29	3.7	14.4	None
262	750	10.2	0.29	6.0	19.5	None
264	700	10.2	0.55	14.0	22.2	None

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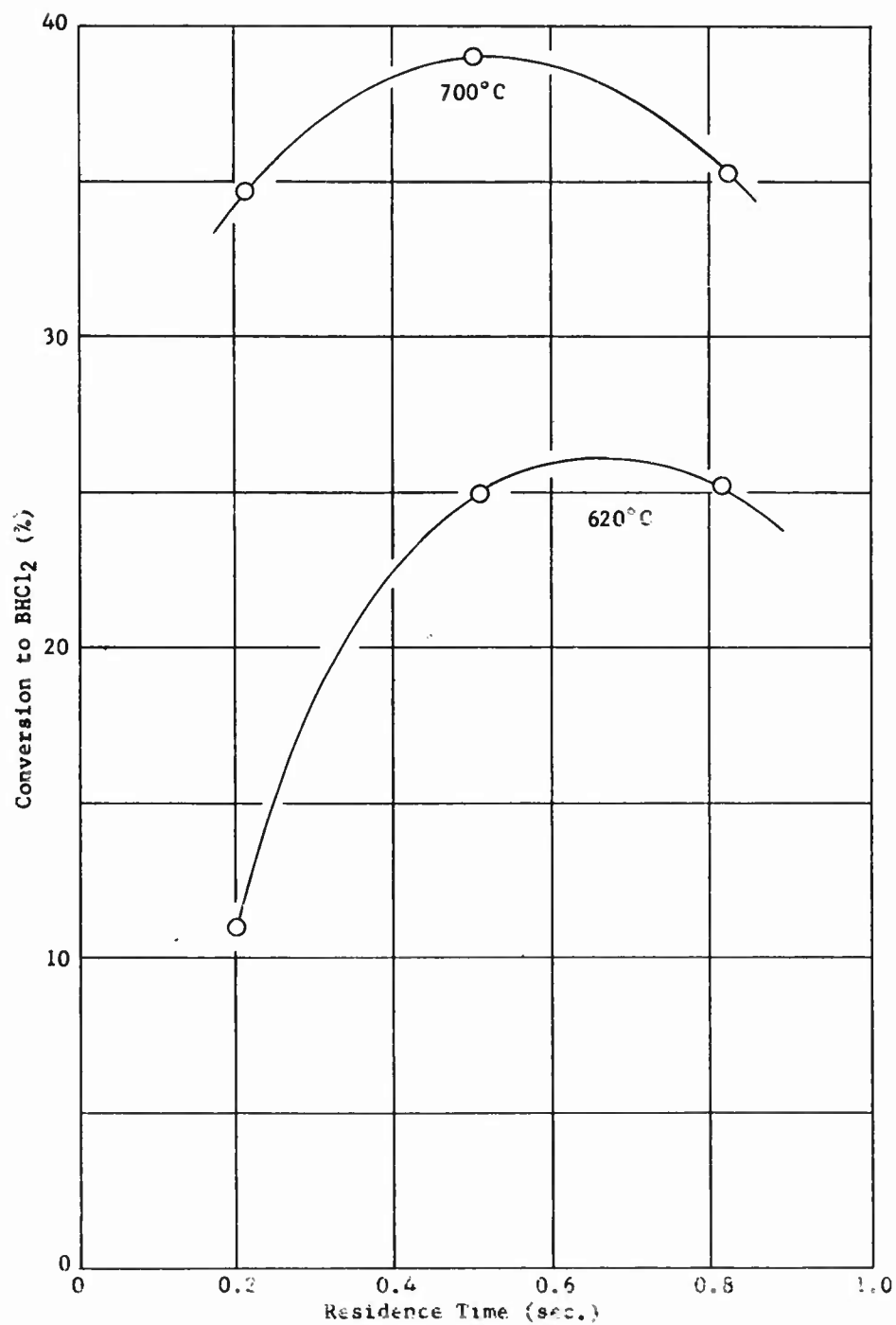


Figure 2. Conversion to BHCl₂ vs. Residence Time
Mole Ratio H₂/BCl₃ = 14; Silver Screen Catalyst

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This permitted the hot gases to enter the cooling zone at a rapid rate and was intended to prevent an equilibrium shift. The results, shown in Table 18, indicated that the equilibrium shift was considerably repressed.

TABLE 18

Hydrogen-Boron Trichloride Reaction Data
Rapid Cooling

Expt. No.	Temp. (°C)	Press. (atm.)	Residence Time (sec.)	Mole Ratio (H ₂ /BCl ₃)	Conv. (%)	Yield (%)
<u>498-</u>						
108	700	1	0.5	15.9	30.3 ^(a)	101.3
110	700	1	0.5	15.9	36.7	101.4
112	700	1	0.8	13.4	35.1	101.0
114	700	1	0.8	13.6	34.5	100.6
121	700	1	0.5	15.6	36.9	100.0
127	700	1	0.5	15.9	35.7	100.8
129	700	1	0.5	15.1	36.3	97.3
131	700	1	0.2	13.9	34.3	101.9
117	750	1	0.5	15.8	37.3	93.4
119	750	1	0.2	12.3	38.2	89.9
133	750	1	0.55	2.75	21.2	101.3

(a) Conditioning experiment.

In this series of runs, temperatures up to 750°C were employed and it was observed that yields began to decline at that temperature, even at the lower residence times. From earlier work, it was believed that higher mole ratios of H₂/BCl₃ increased the tendency toward low yield. The data in Table 18 show that at 750°C when the H₂/BCl₃ mole ratios were reduced to 2.75, there was no lowering of the yield although at higher mole ratios the yield was decreased. Another point of interest is that conversions rose very little in going from 700°C to 750°C. Determinations of conversions and yields were made by chemical analysis. Experimental determinations of the boron balance may have been inaccurate by as much as one or two per cent. When yields were that close to 100 per cent, it was considered that yields were essentially quantitative. This was supported by the fact that under those conditions the IR spectra showed no constituents other than those accounted for in the chemical analysis, and no boron was found on the silver catalyst. On the other hand, when yields were lower, boron was found on the catalyst.

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2. Catalysts and Residence Time

The residence time is defined as the amount of time which the introduced gases spend in the reaction zone, and it is computed as:

$$\frac{\text{Free volume in the reactor zone}}{\text{Volume of flow of gases per second}}$$

The volume of gas flow is based on the temperature and pressure existing in the reaction zone. Since there is no change in the number of moles of gas produced compared to those introduced, no correction for volume change is required in calculating the residence time.

The rate of reaction evidently determines the residence time required to reach equilibrium. Too high a residence time will permit decomposition to boron and consequent loss in yield. There is a limitation, therefore, on residence time. Furthermore, use of a shorter residence time permits the use of a correspondingly smaller reactor. An increase in the rate of reaction will lead to a shorter residence time, and this effect has been accomplished by the use of catalysts; in particular, carbon, copper and silver. The required residence times at atmospheric pressure using silver as a catalyst, compared to the use of a void reactor tube, were found to be much smaller as shown in Figure 13. In Table 19 data are given which show results obtained with different catalysts as well as without catalyst.

TABLE 19

Effect of Catalyst

Expt. No.	Temp. (°C)	Residence Time (sec.)	Mole Ratio (H ₂ /BCl ₃)	Conv. to BHC1 ₂ (%)	Yield of BHC1 ₂ (%)	Catalyst
M-62	700	0.76	14.0	24.4	100.0	None
M-57	700	1.75	14.0	34.1	97.9	None
M-59	700	3.51	15.6	41.8	99.9	None
<u>266</u>						
212	620	0.2	14.0	3.6	-	None
208	620	0.2	14.0	45.0	99.4	Silver
223	620	0.2	14.0	32.1	66.0	Copper
192	620	0.65	14.0	25.6	87.3	Carbon
230	620	0.48	14.0	22.4	72.4	Pd. on C
236	620	0.61	14.0	20.7	57.1	Pt. on C

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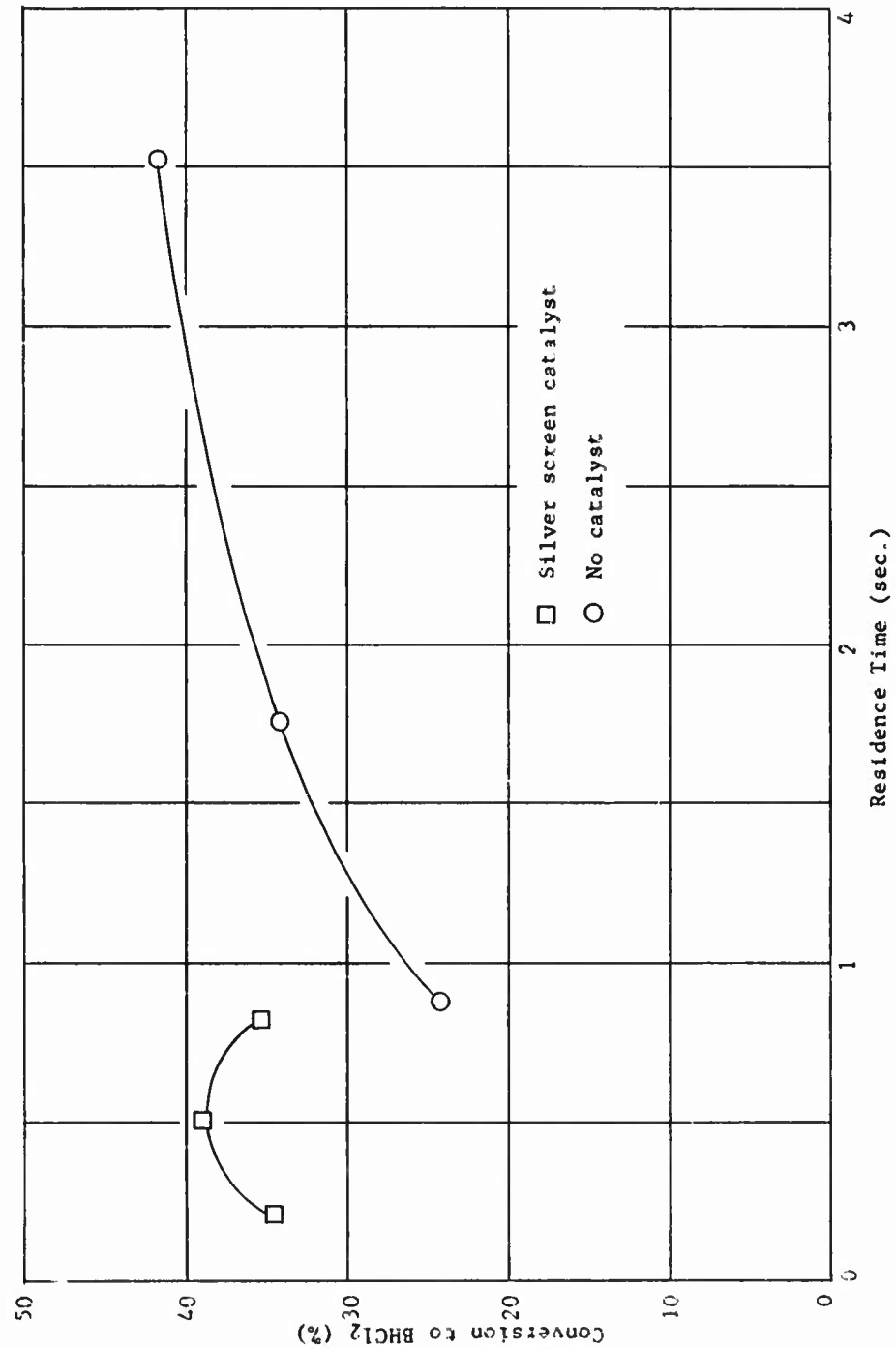


Figure 13. Conversion to BHCl₂ vs. Residence Time
Temp. = 700°C; Mole Ratio H₂/BCl₃ = 14

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Carbon and copper have the undesirable property of reducing the yield, possibly because of boride formation. In the case of copper, an increase in discoloration with continued use is readily observed. With silver, a brownish-black discoloration is observed where the gases enter, but the discoloration appears to progress at a negligible rate, if at all. It is not certain whether this discoloration is due to boron or to impurities in the BCl_3 or H_2 (sulfur compounds, for example). The large bulk of the silver remains bright and silvery through the course of many runs. Silver shows no tendency to induce loss of yield and is consequently the preferred catalyst.

Granular silver of 40 to 60 mesh size gave excellent results at very low residence times, but it has some physical deficiencies; sintering of the silver catalyst was observed to occur. This apparently caused shrinkage of the catalyst bed and consequent channeling of reactor gases through the bed. Successive decreases in conversion for Experiments 498-66, 68 and 70 were attributed to this by-passing of the catalyst by the reaction gases. Experiments 498-72 and -74, which were made after collapsing the glass wall of the reactor to close any channels caused by shrinkage of the catalyst, resulted in higher conversions. This appeared to substantiate the supposition that channeling was responsible for decreased yields. To overcome the channeling problem, silver screens were investigated as catalysts.

When silver screens were substituted for the granular silver catalyst, test runs became more reproducible than had been the case with the granular catalyst. However, higher residence times were required to obtain comparable yields. This effect was evidently due to the lesser surface available.

The catalytic effect of the silver may involve an activation of either the hydrogen or boron trichloride by adsorption on the surface; it also serves as an excellent heat transfer medium to bring the reacting gases quickly to the reaction temperature.

The use of elevated pressure reduces the necessary residence time greatly. This effect would be expected, since it amounts to an increase in concentration of the reactants. Furthermore, heat transfer is greater under pressure. The use of silver catalyst with pressure reduces the required residence time even further. Figure 14 shows the effect of pressure on residence time.

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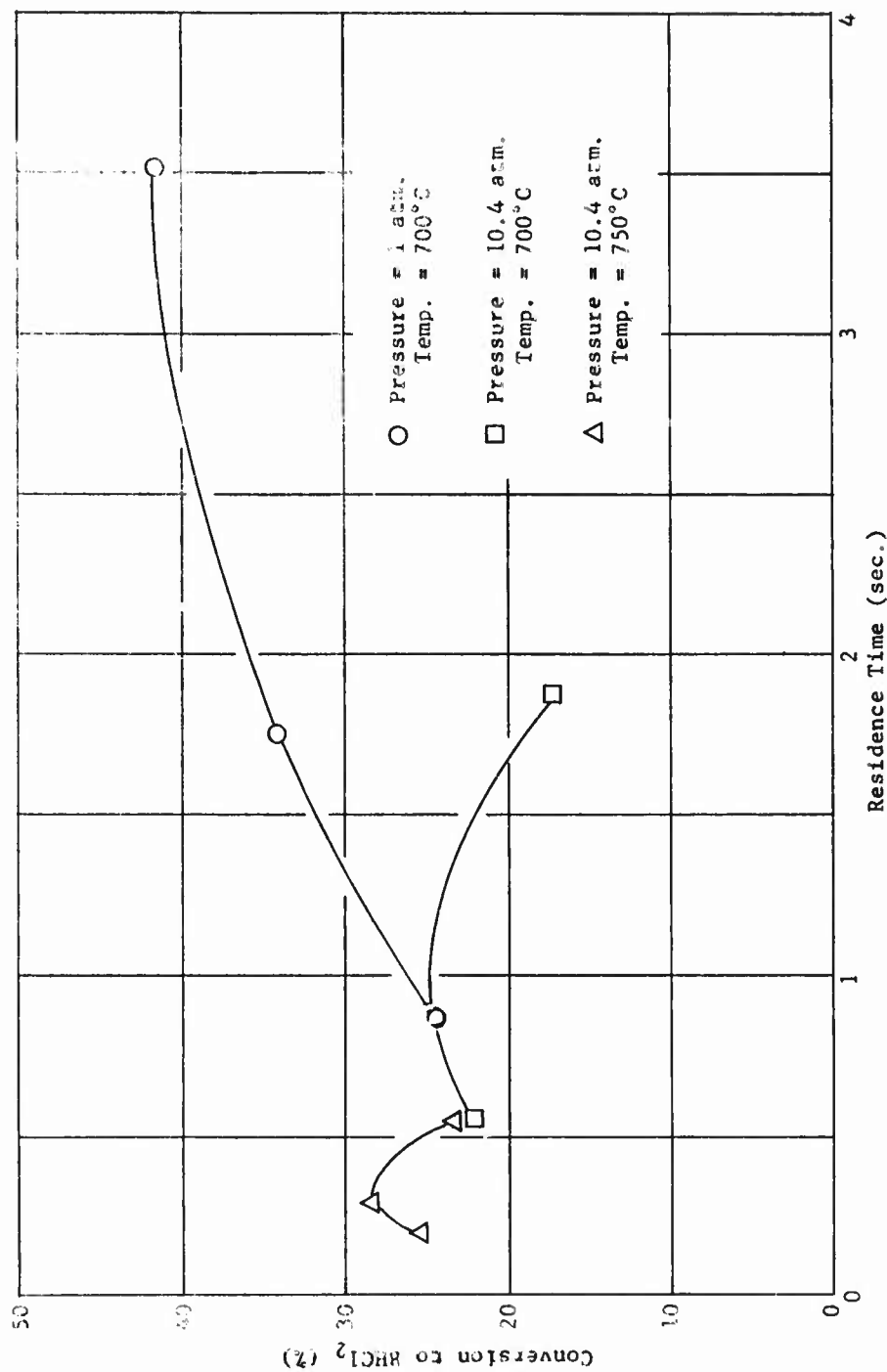


Figure 14. Conversion to BHCl₂ vs. Residence Time
No Catalyst; Mole Ratio H₂/BCl₃ = 14

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3. Molar Ratio of H_2/BCl_3

By the mass reaction effect, an increase in the molar ratio of H_2/BCl_3 should increase the conversion of BCl_3 to $BHCl_2$. Conversely, a decrease in the molar ratio of H_2/BCl_3 should give a higher conversion of H_2 to $BHCl_2$. The experimental results, depicted in Figure 15, show these effects very clearly.

In the earlier work the molar ratio of H_2/BCl_3 was adjusted by bubbling H_2 gas at a metered flow rate through liquid BCl_3 maintained at a temperature corresponding to the partial pressure desired in the H_2 stream. However, it was later found that this system gave inadequate control of the mixture ratio because of incomplete saturation of the H_2 with the BCl_3 and because of fluctuations in the temperature. As a result of these difficulties, the bubbling device was eliminated and the reactants (H_2 and BCl_3 gas) were metered separately into a mixing chamber before being fed into the reactor. This change led to more consistent results. The earlier results tended to give higher conversion values because the error was always toward higher H_2/BCl_3 ratios than intended.

At $700^\circ C$ the conversion at a molar ratio of 3 is about 20 per cent and at a molar ratio of 14, it is about 39 per cent. At the higher mole ratio the total amount of gas carried along per mole of $BHCl_2$ formed is almost twice as great. This means that at the higher mole ratio larger equipment is required, the heating and cooling loads are greater, and, finally, the difficulties in separating the BCl_3 , $BHCl_2$ and HCl from the H_2 are greater because they are present at lower partial pressures. On the other hand, at the lower mole ratio almost twice as much BCl_3 is present per mole of $BHCl_2$ formed as is present at the higher mole ratio. This can lead to greater difficulties in the disproportionation step which benefits from lower concentrations of BCl_3 . The optimum mole ratio was therefore based on engineering design evaluations as well as pilot plant studies.

4. Effect of Pressure

Since the reaction equation shows the same number of molecules on the left as on the right, it might be expected that pressure would not exert a great influence on the extent of conversion. On the other hand, because of the increased concentration effect, a faster reaction rate would be anticipated. Experiments at 10.2 atmospheres have shown increased reaction rate (Figure 14) but the conversions in general have been lower.

It is highly unlikely on theoretical grounds that pressure itself was responsible for the reduced conversions, and a more reasonable explanation is possible. Since reaction rates are shown to be much higher under pressure conditions, it is to be expected that the back reaction would also take place faster. Consequently, quenching

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(rapid cooling) of the reaction gases may be much more critical under pressure conditions. In other words, the conversions in the reactor zone may have been as high as those obtained without pressure, but the rate of cooling of the gases relative to the higher reaction rates under pressure may have been inadequate to prevent shifting of the equilibrium to the left. The observation of reduced conversions with higher residence times has already been referred to with respect to reactions at atmospheric pressure (Figure 12). It will be noted that this effect is considerably more pronounced under pressure (Figure 14) and tends to confirm the argument given previously.

B. Back Reactions of BHCl_2 and HCl

To determine the rate at which reaction gases must be quenched to prevent a diminution of the conversion, equipment was set up to study the rate of back reaction of BHCl_2 with HCl at different temperatures. The reaction mixture, emerging from the reactor at 700°C , was divided into two streams; one being passed through a controlled temperature coil and the other, the bypass, quenched with liquid nitrogen to remove the condensable materials. The gases leaving the coil were also cooled with liquid nitrogen to condense the reaction products. The temperature of the coil and residence time of the gases passing through it could be controlled. The products from the coil and from the bypass were then analyzed to compare the respective amounts of dichloroborane present. Results are given in Table 20.

TABLE 20
Conversion of Reaction Gases^(a)

Expt. No.	Conv. in Reactor (%)	Coil Temp. ($^\circ\text{C}$)	Residence Time in Coil (sec.)	Conversion after Coil (%)
485-181	19.3	400	1.38	19.7
485-184	16.5	400	2.82	16.2
485-190	17.7	400	5.13	15.7
486-209	16.7	400	5.05	15.2
486-197	16.5	400	10.53	16.0
486-212	16.8	400	11.25	16.1
486-206	16.5	400	11.80	15.0
486-219	17.6	500	31.68	12.3
486-215	17.0	500	36.75	12.3
486-222	17.3	500	29.53	11.9
486-233	16.51	500	7.49	14.43
486-226	16.68	500	17.30	13.43
486-222	17.28	500	29.53	11.86
486-247	18.05	400	52.66	15.12
486-262	17.91	400	24.80	16.67
486-242	18.09	400	11.04	17.39

(a) Reactor temp. 700°C , mole ratio $\text{H}_2/\text{BCl}_3 = 2.75$ to 3.19 .

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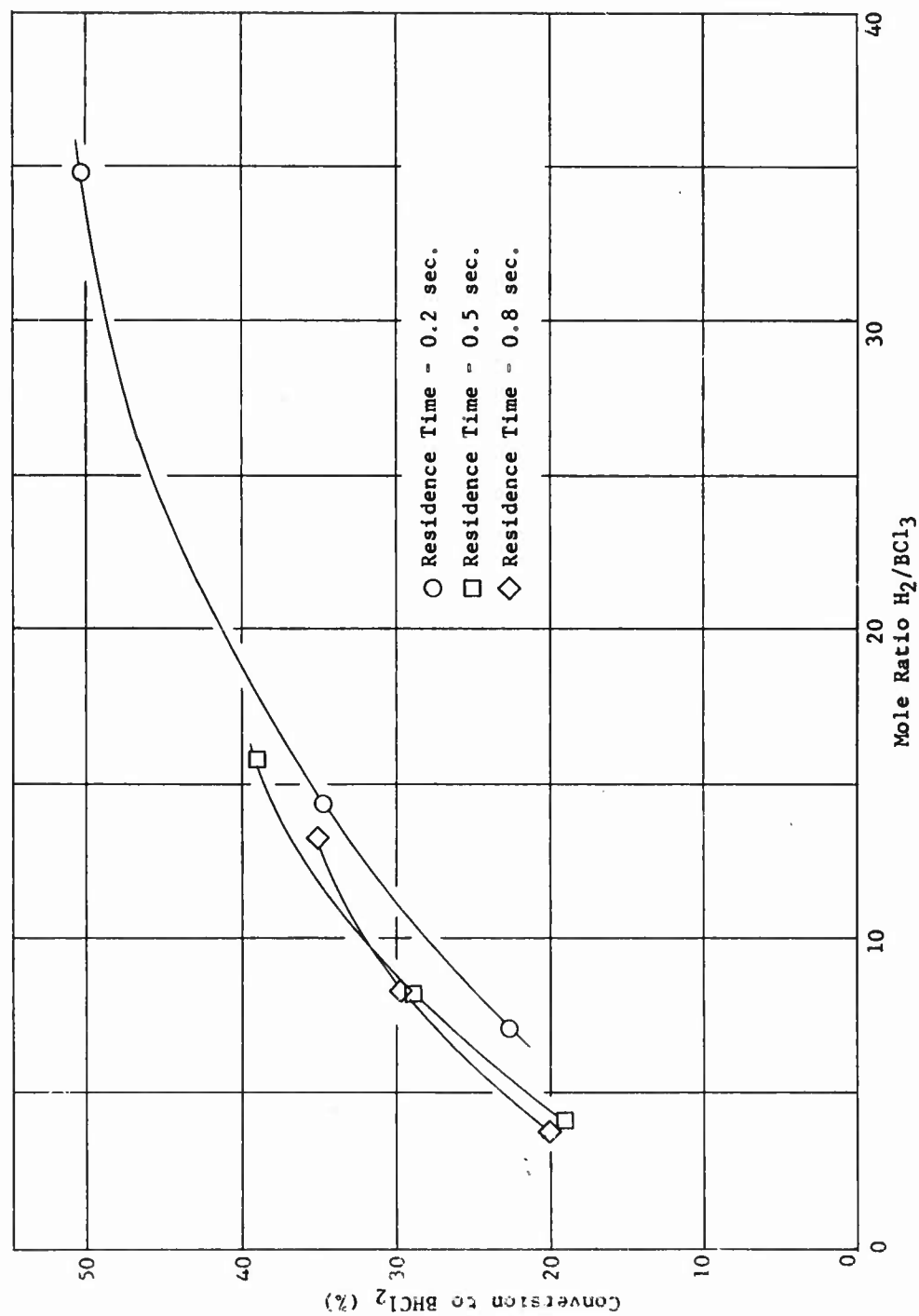


Figure 15. Conversion to BHC12 vs. Mole Ratio
Temp. = 700°C; Silver Screen Catalyst

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Back reaction data at temperatures near ambient were obtained by following BHCl_2 disappearance in an infrared cell. In these experiments, samples of BHCl_2 and BCl_3 were placed in a one centimeter IR cell and the partial pressure of BHCl_2 determined by infrared analysis. The cell was then pressurized with HCl , and the rate of consumption of BHCl_2 was followed by measuring the optical density of BHCl_2 at 9.12 microns. The reaction rates were measured at 25.6°C , at 30.6°C and $53.0^\circ\text{C} \pm 1.0^\circ\text{C}$. The data obtained in a typical experiment are shown in Table 21.

TABLE 21

Back Reaction Data Near Ambient Temperature

Infrared Cell: 10.5 mm.
Pressure of BCl_3 + BHCl_2 Before Addn. of HCl : 149 mm.
Partial Pressure of BHCl_2 as Determined by IR: 13.30 mm.
Total Pressure After Addn. of HCl : 332 mm.
Infrared Cell Temperature: $53^\circ\text{C} \pm 1.0^\circ\text{C}$

Time (min.)	0	9	13	17	27	36	48
Pressure BHCl_2 (mm. Hg.)	13.30	13.24	13.14	13.09	12.88	12.78	12.46

Rate constants for the back reaction were calculated from these data and are listed in Table 22. From the slope of the Arrhenius plot (Figure 16) of $\log k$ vs. $1/T^\circ\text{K}$ the activation energy for the back reaction was found to be 9.1 kcal/mole.

TABLE 22

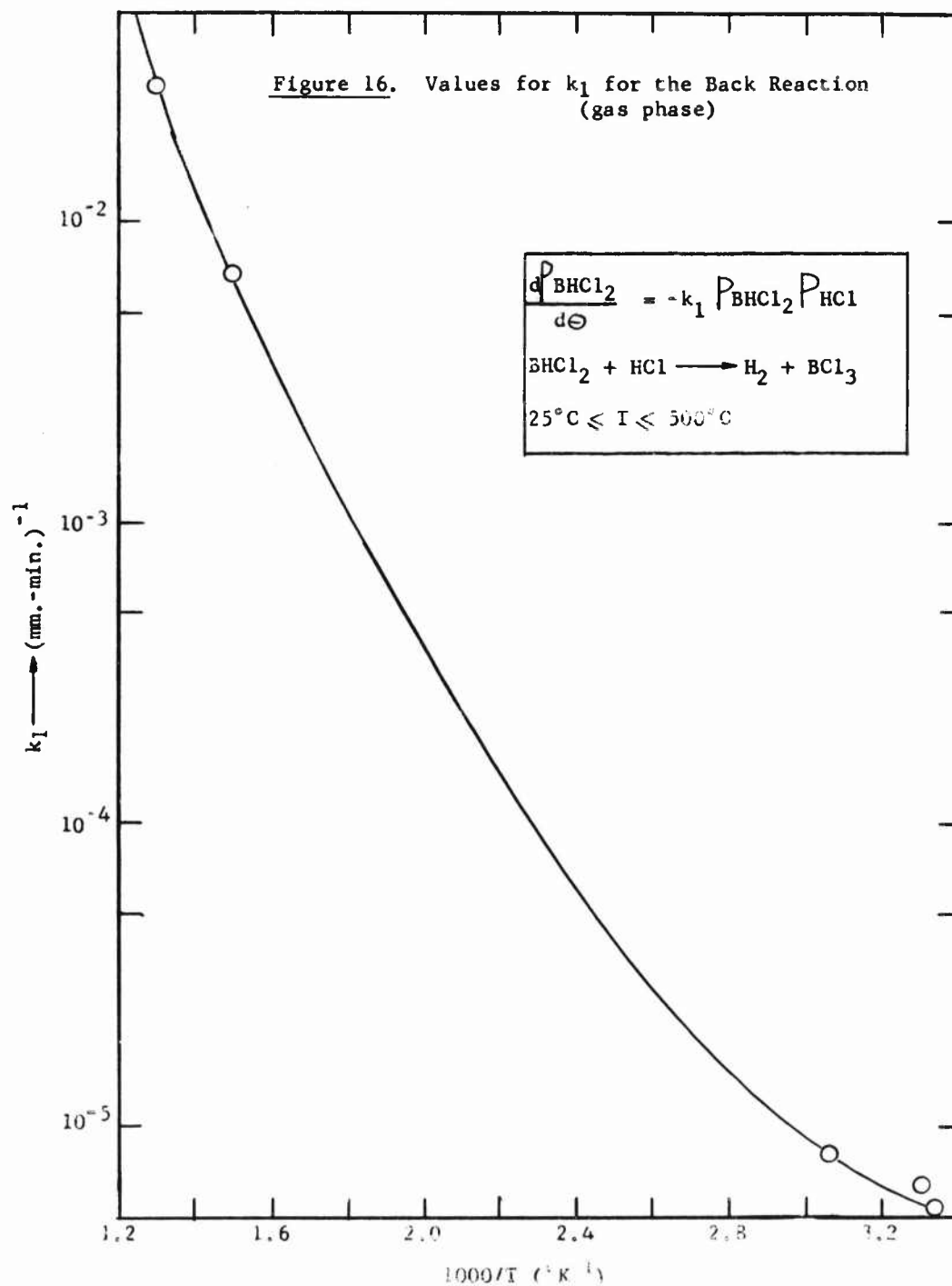
Rate Constants for Back Reaction

Temp. ($^\circ\text{C}$)	Reaction Rate Constant k	
	(mm.-min.) $^{-1}$	liter/mole-sec.
25.6(a)	5.43×10^{-6}	2.74×10^{-6}
30.6(a)	6.64×10^{-6}	2.74×10^{-6}
53(a)	8.36×10^{-6}	3.71×10^{-6}
400(b)	6.75×10^{-3}	6.20×10^{-3}
500(b)	2.88×10^{-2}	3.04×10^{-2}

- (a) The reaction rate was followed by BHCl_2 disappearance as measured by IR.
(b) The reaction rate was followed by consumption of active hydrides, as determined by evolution of H_2 on hydrolysis, both before and after the coil.

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The magnitude of these rate constants is such that rapid quenching, i.e., within a few seconds, is necessary for best reactor productivity and minimum change from the favorable high temperature equilibrium.

C. Apparatus and Procedures

In the early studies with silver catalyst, a reactor made of Corning No. 1740 ignition glass was employed. This reactor was "U" shaped, with an inlet arm smaller in diameter than that of the reactor arm, and contained a thermocouple well. The reactor portion contained 40.6 grams of granular silver (about 30 mesh) in about 10 mls. The total heated volume was about 30 mls. A flow meter measured the rate at which H₂ passed first through heated copper to remove oxygen, then through a liquid N₂ cooled trap to remove water. Then the H₂ was passed through a bubbler containing liquid BCl₃. The temperature at which the boron trichloride was maintained determined the amount of BCl₃ in the H₂. The gas then passed into the reactor which was inside an electrically heated oven. The emerging product was captured in a train of three traps cooled by liquid N₂.

Later work employed a Vycor reactor with an exit tube having a small diameter to allow exhaust gases to escape the hot zone as rapidly as possible. The reactor was a straight tube design with thermocouple well, was 4.5 inches long, and contained 35 grams of silver screen. The inside diameter of the exit and inlet tubes was 5 mm. The total heated reactor volume was 16.2 mls. and the free volume was 11.7 mls. Boron trichloride and hydrogen were separately metered through rotameters. The boron trichloride was taken from a small cylinder which could be weighed before and after the experiment.

The studies under elevated pressure were conducted in two different stainless steel tube reactors. One was 10.2 cms. long and with 0.8 cm. I.D.; the other was the same length but 0.635 cm. I.D. The reactions were studied both with an empty tube (no catalyst) and with silver granules filling the tube. A flow meter measured the H₂ flow following the reactor and collecting traps. The BCl₃ was picked up by the H₂ passing through liquid BCl₃ in a stainless steel bubbler, and the amount of BCl₃ determined by the temperature. The H₂ was pretreated as before and the exhaust gases were collected in traps cooled by liquid N₂ as before.

The conversions and yields, as referred to in this report, are expressed by:

$$\% \text{ Conversion} = \frac{\text{BHCl}_2 \text{ produced}}{\text{Total BCl}_3 \text{ introduced per pass}} \times 100$$

$$\% \text{ Yield} = \frac{\text{H}_2 \text{ evolved on hydrolysis}}{\text{Boron consumed}} \times 100 = \frac{\text{BHCl}_2}{\text{BHCl}_2 + \text{B lost}} \times 100$$

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III. Separation Processes

Economic considerations require efficient recovery of each of the four components of the reactor effluent in pure form as product, by-product or recycle reactant.

Four separation schemes were studied: gaseous diffusion, adsorption on carbon, absorption by complexing, and absorption by an inert liquid.

A. Gaseous Diffusion

No experimental work was conducted on diffusion as a separation process, but a theoretical feasibility study was performed. The diffusion process can be designed to reduce the hydrogen accompanying the other components to any degree economically feasible. Subsequent steps to separate the other components from each other and from any residual hydrogen are then necessary, and might take the form of a distillation or liquid absorption process, for example. This subsequent step, however, becomes a far simpler and less costly procedure when the bulk of the hydrogen has been removed.

Of the various diffusion methods of gas separation, such as mass diffusion, thermal diffusion and gaseous diffusion, an example of separation of hydrogen by gaseous diffusion was worked out to demonstrate the feasibility of such separations in the process under consideration.

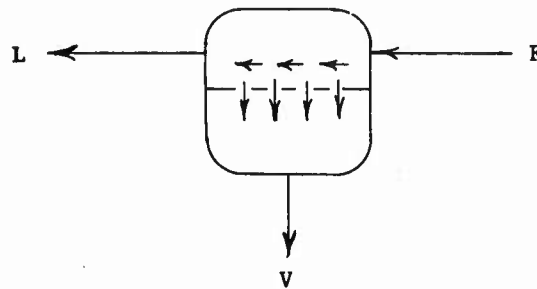
For this problem, a diffusion stage was conceived as operated with the flow of gas parallel to the barrier at the high pressure side with a constantly changing gas composition as selective diffusion occurs, and with the flow of gases away from, or perpendicular to, the barrier at the low pressure side to give an averaged gas concentration exiting (Figure 17). Under the conditions of this problem, a three-stage countercurrent separation was found desirable for illustrative purposes (Figure 18).

By material balance and use of the chart of Figure 19, a three-stage countercurrent separation problem was worked out as shown by the data of Table 23 and Figure 18. Average concentrations and average molar velocities were used for each stage rather than the more accurate incremental concentrations and velocities because equations derived for accurate solution were in a differential form and have not been successfully integrated. The averages used were accurate enough, however, to give the barrier surface requirements for the two sets of pressure conditions (Table 24).

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L = Effluent gas - high pressure side
V = Effluent gas - low pressure side
F = Feed gas

Figure 17. Illustrative Gas Flows in Diffusion Cell or Stage

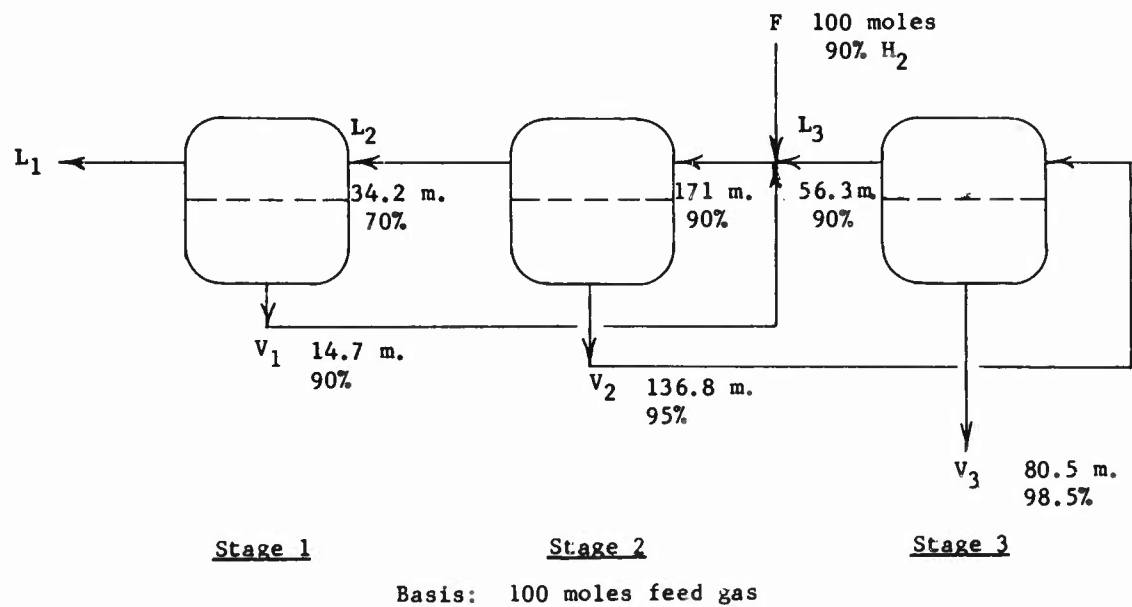


Figure 18. Molal Material Balance and Hydrogen Concentrations for Three-Stage, Countercurrent Flow, Diffusion Cascade

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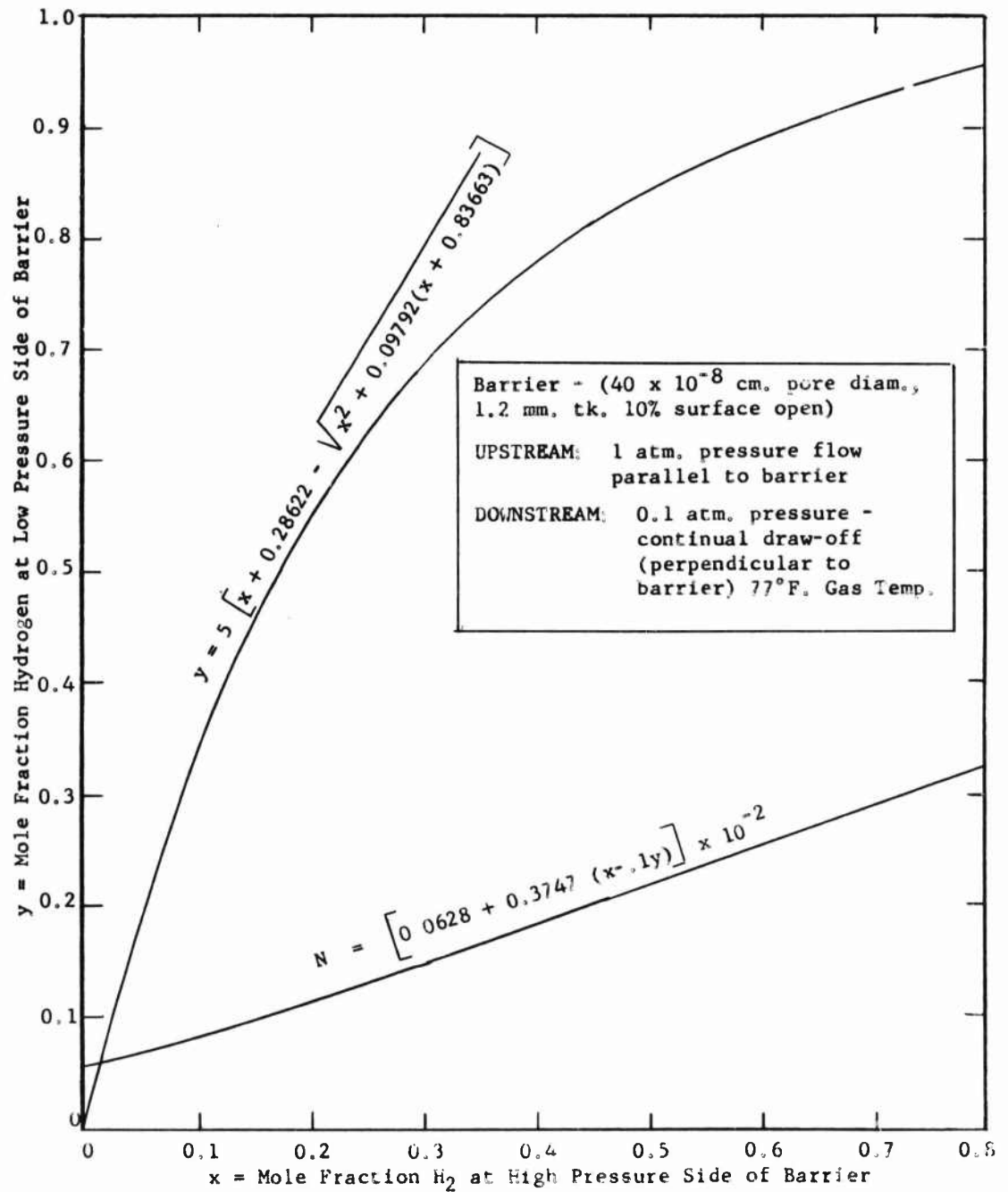


Figure 19. Gaseous Diffusion of Hydrogen and Other Gases (Av. M.W. 81.5) Through Porous Glass

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TABLE 23

Material Balance for Gaseous
Diffusion Separation of Pilot Plant Quantities

	<u>M.W.</u>	<u>Mole %</u>	<u>Moles/Hr.</u>	<u>Lbs./Hr.</u>	<u>Wt. %</u>
<u>Feed Gas (F)</u>					
Hydrogen	2.016	90	5.076	10.2	18.2
Other Gases	81.5	10	0.564	46.0	81.8
(Precursor)	<u>(82.74)</u>	<u>(3)</u>	<u>(0.169)</u>	<u>(14.0)</u>	<u>(24.9)</u>
Total		100	5.640	56.2	100.0
<u>High Press. Discharge (L₁)</u>					
Hydrogen		55	0.605	1.2	2.9
Other Gases		45	0.495	40.4	97.1
(Precursor)		<u>(13.5)</u>	<u>(0.1485)</u>	<u>(12.3)</u>	<u>(29.6)</u>
Total		100	1.100	41.6	100.0
<u>Low Press. Discharge (V₃)</u>					
Hydrogen		98.5	4.472	9.0	61.9
Other Gases		1.5	0.068	5.6	38.1
(Precursor)		<u>(0.45)</u>	<u>(0.0204)</u>	<u>(1.7)</u>	<u>(11.6)</u>
Total		100.0	4.540	14.6	100.0
<u>Separation</u> <u>Quantities</u>	<u>Vol. %</u> <u>of F</u>	<u>Wt. %</u> <u>of F</u>	<u>% of</u> <u>Total H₂</u>	<u>% of Total</u> <u>Precursor</u>	
Low Pressure Effluent, V ₃	80.5	26	88.1	12.1	
High Pressure Effluent, L ₁	<u>19.5</u>	<u>74</u>	<u>11.9</u>	<u>87.9</u>	
Feed Gas, F	100.0	100	100.0	100.0	

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TABLE 24

Calculated Area Requirements For Diffusion Barriers for Pilot Plant

Arrangement: Three-Stage Countercurrent Flow
Porous Barrier: Vycor Glass Intermediate, 1.2 mm. Thick
Feed Gas: 5.64 moles/hr., 90% Vol. % H₂, 10% Other Gases (M.W. 81.5),
or 0.61 ft.³/sec. feed flow volume at 77°F.

Stage	Volume % H ₂ in Gas			Moles/Hr. Gas L.P. Out	Calculated Area	
	H.P. In	H.P. Out	L.P. Out		H.P. 1 atm. L.P. 1 atm.	10 atm. 1 atm.
1	70%	55%	90%	0.82	316 ft. ²	32 ft. ²
2	90%	70%	95%	7.72	2,374 ft. ²	237 ft. ²
3	95%	90%	98.5%	4.54	<u>1,222 ft.²</u> 3,912 ft. ²	<u>123 ft.²</u> 392 ft. ²

H.P. = High Pressure Side of Barrier in Stage.
L.P. = Low Pressure Side of Barrier in Stage.

As shown, the three-stage separation removed 88 per cent of the H₂ in the feed with a loss of about 12 per cent of the other gases (or BHCl₂ since its molecular weight is close to the average of the non-hydrogen gases). That is, a given feed gas of 90 per cent hydrogen by volume (18.2% by wt.) was separated into two fractions: a high pressure fraction, 19.5 per cent of the feed volume (74% of the feed by wt.), that contained 55 per cent H₂ by volume (2.9% by wt.); and a low pressure fraction, 80.5 per cent of the feed volume (26% of the feed wt.), that contained 98.5 per cent H₂ by volume (61.9% by wt.). Such a separation could be of appreciable importance in recovery and purification of dichloroborane.

Research testing of diffusion barriers, those available and new ones, would be the prime requirement for developing this separation method for use in this high energy fuel process at a cost competitive with other processes.

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B. Adsorption on Carbon

The recovery of boron trichloride by adsorption on carbon was worked out as a process by the Hooker Electrochemical Company in order to separate boron trichloride from hydrochloric acid in the presence of large amounts of hydrogen. However, under their best conditions they obtained a significant loss of boron trichloride on every adsorption-desorption cycle. This loss would render the process completely impossible for the present application.

Following the procedures of Hooker Electrochemical, with minor variations, it was found that at 15°C prechlorinated activated Columbia Carbon, CXA pellets, adsorbs an amount of boron trichloride equivalent to 44.6 per cent of the weight of the carbon. Similarly, Columbia PW Carbon, pretreated with boron trichloride, retained 50 per cent of its weight of boron trichloride at 0°C under about 27 mm. partial pressure of boron trichloride. However, as with Hooker there was a significant, irretrievable loss of boron trichloride on desorption. Since this desorption was conducted at 170 to 200°C, it was decided that the high temperature was causing a chemical reaction which destroyed the boron trichloride. By employing a maximum desorption temperature of 100°C for an arbitrary period of time (2 hrs.) about 80 per cent of the boron trichloride is desorbed. However, on repeating the adsorption-desorption cycle in this manner it was found that 100 per cent of the boron trichloride adsorbed on the second cycle was desorbed.

The same technique was then applied to the adsorption and desorption of BHCl_2 . On a first cycle of a mixture of BHCl_2 and BCl_3 , followed by desorption at 100°C, no BHCl_2 was recovered. However, it was expected that a certain build-up of BHCl_2 content on the carbon would be required before it would start to come off at the arbitrarily set condition of 100°C desorption temperature. The carbon was then treated with diborane at 100°C to react with any impurities that might attack a boron hydride. On a second cycle with a BCl_3 - BHCl_2 mixture, desorption at 100°C for one hour gave a recovery of 22 per cent of the BHCl_2 adsorbed. This was the first instance of successful desorption of BHCl_2 from carbon. It is believed that on further cycling, 100 per cent desorption might occur. This work was discontinued because it was considered that the liquid absorption methods would be more desirable.

C. Absorption by Complexing

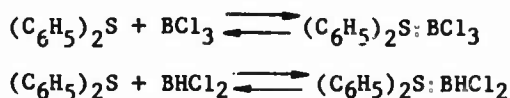
1. Diphenyl Sulfide

Another separation process, absorption by complexing, involves the use of a chemical bonding substance. After study of a number of such substances, diphenyl sulfide, $(\text{C}_6\text{H}_5)_2\text{S}$, was found to form a solid adduct with both boron trichloride and dichloroborane, thus making possible their

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removal from the hydrogen and hydrogen chloride. The reactions for the adducts formation are shown below:



Complexing studies of diphenyl sulfide with boron trichloride and dichloroborane at 0°C were investigated by bubbling a gas stream containing boron trichloride, dichloroborane, hydrogen chloride and hydrogen through a solution of diphenyl sulfide in a saturated aliphatic oil (Brillol). The diphenyl sulfide-oil solution retained most of the boron containing compounds while allowing the hydrogen chloride and hydrogen to pass through. A small amount of boron trichloride was carried along with the hydrogen. The hydrogen chloride and residual boron trichloride were separated from the hydrogen by condensation at -196°C. Heating the diphenyl sulfide-oil solution under reduced pressure at 80 to 150°C generated BHCl₂, BCl₃ and B₂H₆. Hydrolysis of the products and determination of the hydrogen evolved and boron contents gave the results shown in Table 25.

TABLE 25

Absorption of BCl₃ and BHCl₂ by Diphenyl Sulfide

Expt. No.	Init. BCl ₃ Hydro-generated (mmol)	Absorption(a) Medium		Desorbed(b) from (C ₆ H ₅) ₂ S		Condensables(d) in Effluent Gas			B Recovery (%)
		(C ₆ H ₅) ₂ S (mmol)	Oil(b) (mmol)	BHCl ₂ (mmol)	BCl ₃ (mmol)	BHCl ₂ (mmol)	BCl ₃ (mmol)	HCl (mmol)	
486-40	21.15	193.0	0.0	4.08	15.44	0.00	0.75	5.69	96.2
486-42	11.31 ^(e)	193.0	0.0	1.67	6.65	0.0	1.38	2.90	85.9
486-59	13.44	21.5	20.2	3.41	7.95	0.0	1.99	3.90	99.3

(a) Absorption was carried out at 0°C.

(b) Avg. molecular wt. = 253.

(c) Desorption was carried out at 80-150°C under reduced pressure.

(d) Amounts condensed, at -196°C, from the H₂ stream.

(e) Absorption was carried out at 25°C.

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The absence of BHCl_2 in the effluent gas indicates that the BHCl_2 -diphenyl sulfide complex is more stable than the BCl_3 -diphenyl sulfide adduct and, most important, that the desired separation of BHCl_2 from HCl is efficiently accomplished.

The recovery of dichloroborane and boron trichloride from their adducts with diphenyl sulfide was investigated. A temperature of 151°C was required to obtain a vapor pressure of one atmosphere (752 mm. Hg.) above the solution of diphenyl sulfide adduct. The following data were collected on the composition of the vapor and liquid phases:

Thermal Recovery of BHCl_2 and BCl_3

	Original Liquid Composition (millimoles)	Liquid Composition at 151°C and 752 mm. Hg. (millimoles)	Vapor Composition at 151°C and 752 mm. Hg. (millimoles)
$(\text{C}_6\text{H}_5)_2\text{S}$	141.7	141.7	-
BHCl_2	7.34	4.91	2.43
BCl_3	13.27	3.33	9.94

These data confirmed the fact that dichloroborane is held more tenaciously than boron trichloride. Furthermore, they indicate that unless a carrier vapor or vacuum is employed, high temperatures are required to recover the boron compound.

The dissociation pressures of the diphenyl sulfide-boron trichloride adduct at various temperatures were experimentally determined:

Dissociation Pressures of $(\text{C}_6\text{H}_5)_2\text{S}:\text{BCl}_3$

Temp. ($^\circ\text{C}$)	0	11	14	19	23.5	24.5	28.9	33.9	36.4	37.6	46
Press. (mm. Hg.)	1	4	5	9	15	20	30.5	48	64	74	189.5

The plot of $\log P$ vs. $1/T$ is shown in Figure 20. The equation for the dissociation pressure, calculated by the method of least squares, is

$$\log_{10} P_{\text{mm.}} = \frac{-4251}{T} + 15.2605$$

from which the heat of dissociation can be calculated to be 19.5 Kcals/mole, and it is found that a pressure of one atmosphere is reached at 70°C .

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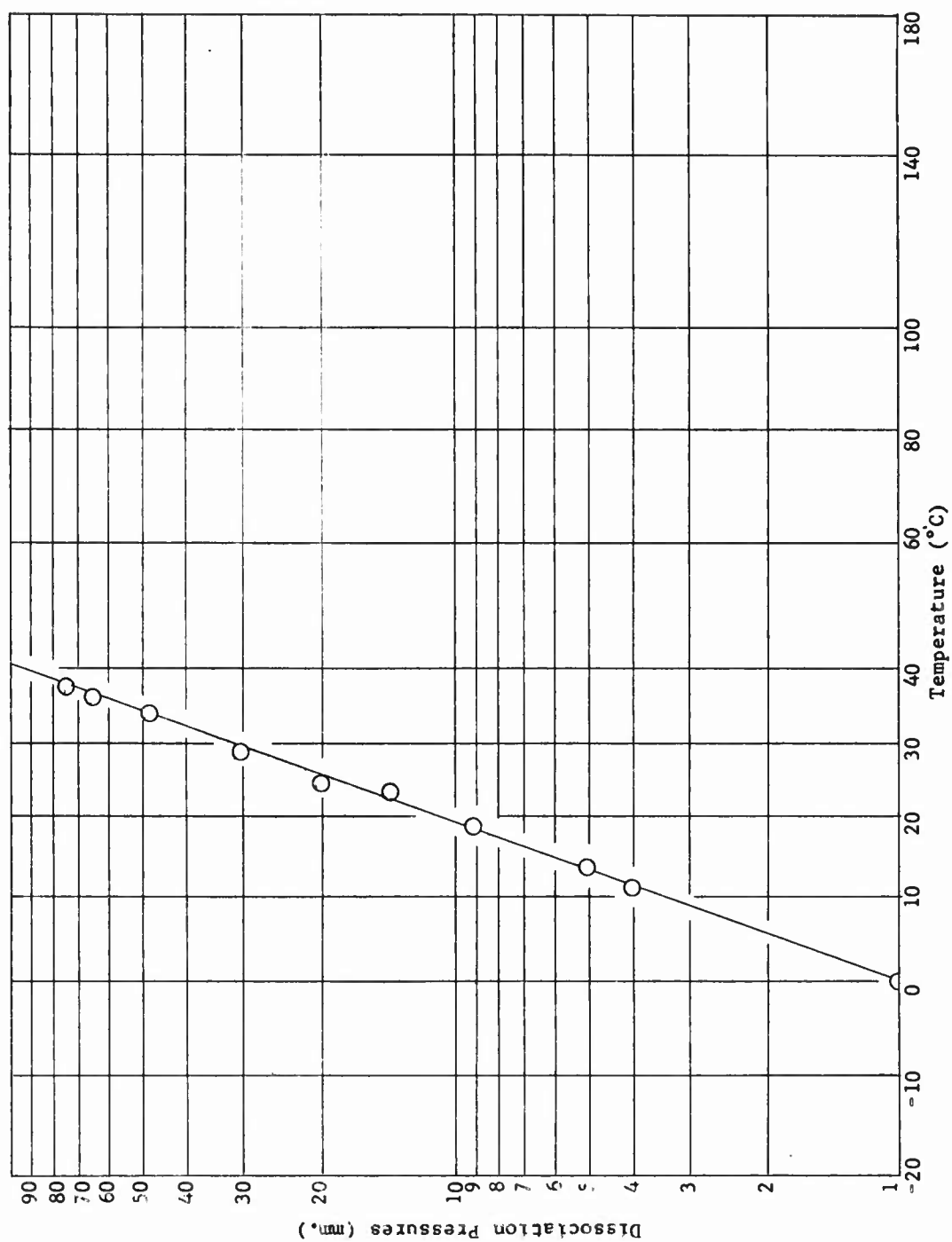


Figure 20. Dissociation Pressures of the 1:1 Adduct $(C_6H_5)_2S:BCl_3$

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Because of the low vapor pressure of diphenyl sulfide, the vapor phase consisted essentially of pure boron trichloride. These values of the dissociation pressure are only approximate since the liquid composition changed during the dissociation because of the boron trichloride released into the gas phase. It is estimated that a 7 per cent excess of diphenyl sulfide was present when the pressure reached 100 mm.

The adduct formed by the addition of dichloroborane to diphenyl sulfide is a white solid having no appreciable volatility at 0°C. It begins to melt at about 42°C with dissociation.

The dissociation pressures of $\phi_2\text{S}:\text{BHC1}_2$ were determined by measuring the pressure developed over a range of temperature. To obtain a greater degree of accuracy, the vapor volume was made as small as possible, thereby avoiding any significant change in the liquid composition. Furthermore, to overcome the effect of disproportionation of the BHC1_2 , the vapor phase was also maintained at elevated temperature. Thermodynamic calculations have shown that the extent of disproportionation of BHC1_2 is decreased at elevated temperatures. The sample employed for the measurement of the dissociation pressures was found to have a molar ratio of diphenyl sulfide to BHC1_2 of 1.05. The results are shown below.

Dissociation Pressures of $(\text{C}_6\text{H}_5)_2\text{S}:\text{BHC1}_2$ Adduct

Temp. (°C)	69.5	72.3	74.2	76.0	79.2	81.7
Pressure (mm. Hg.)	1063	1102	1259	1375	1462	1505

The remainder of the BHC1_2 was removed from the diphenyl sulfide by heating under vacuum. The residual diphenyl sulfide was found to have an infrared spectrum identical with that of a pure sample. In spite of heating at 130°C to 140°C for 3.5 hours in the presence of BHC1_2 , BCl_3 and B_2H_6 , the diphenyl sulfide showed no signs of decomposition.

It was considered possible that the diphenyl sulfide might catalyze the back reaction, as follows:



and, in fact, the first two experiments, recorded in Table 25, show reduced conversions of 19.4 per cent and 16.2 per cent, respectively. However, the diphenyl sulfide in these experiments was present in great excess (ratios of 9.2 and 17.1, respectively). At lower diphenyl sulfide to boron ratios, as seen in Table 26, no back reaction is observable at a ratio of $\phi_2\text{S}:\text{B}$ of 0.84, but about 14 per cent back reaction is observed at a ratio of 1.60.

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TABLE 26

Effect of Diphenyl Sulfide on Conversion

Expt. No.	BCl ₃ Hydro- genated (mmol)	Mole Ratio Ø ₂ S/B in Gas Mixt. (mmol)	B Recovery from (C ₆ H ₅) ₂ S (%)	Over-All Conversion to BHCl ₂	
				with (C ₆ H ₅) ₂ S ^(a) (%)	without (C ₆ H ₅) ₂ S (%)
486- 54	15.10	0.84	100.0 ^(b)	28.7	27.7
486- 59	13.44	1.60	100.0 ^(b)	25.5	29.7

- (a) Per cent over-all conversion was based on active hydride content after recovery from diphenyl sulfide.
(b) Analysis of the diphenyl sulfide after desorption showed absence of boron, active hydride and hydrogen chloride.

In order to obtain kinetic data which would permit design of an absorber capable of minimizing the back reaction, measurements of the rate of back reaction were made at different partial pressures of HCl. The adducts, Ø₂S:BHCl₂ and Ø₂S:BCl₃ were prepared by bubbling the exit gases from the reactor through diphenyl sulfide or diphenyl sulfide-oil solution at 0°C. The resulting diphenyl sulfide solution or slurry, containing the partly dissolved adducts with an excess of diphenyl sulfide, was then mixed with hydrogen chloride in a closed system at different partial pressures of HCl for definite periods of time. At the end of each time interval, the hydrogen evolved and was measured after being separated from the unreacted hydrogen chloride. The data are shown in Table 27 and plotted in Figure 21.

These data show that the rate of reaction at 0°C of HCl with the diphenyl sulfide-oil slurry is decidedly affected by the partial pressure of the HCl over the system.

The experiment in which diphenyl sulfide was used in large excess (to dissolve the adduct completely) showed a faster rate of reaction than did the experiment at comparable HCl pressure but with a smaller amount of diphenyl sulfide. The effect of increased partial pressure of HCl is greater than an increase in the amount of diphenyl sulfide.

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TABLE 27

Reaction of Hydrogen Chloride with $(C_6H_5)_2S:BHCl_2$ Adduct

Expt. No.	Press. HCl (mm.)	Initial Composition of Reaction Mixt.			
		$(C_6H_5)_2S$ (mmol)	Oil (mmol)	BCl_3 (mmol)	$BHCl_2$ (mmol)
I	58-60	19.35	19.82	5.50	5.15
II	279-295	29.85	29.70	8.38	4.86
III	59-60	141.70	0.0	12.85	7.76

<u>Time of Shaking with HCl (min.)</u>	<u>Hydrogen Evolved (Cumulative Amt. millimoles)</u>	<u>$BHCl_2$ Consumed (%)</u>

Experiment I

1	0.009	0.175
4	0.020	0.388
10	0.031	0.602
20	0.041	0.776

Experiment II

1	0.14	2.88
4	0.39	8.03
10	0.64	13.15
19	0.98	20.15

Experiment III

1	0.118	1.50
4	0.165	2.14
10	0.275	3.57
19	0.381	4.94

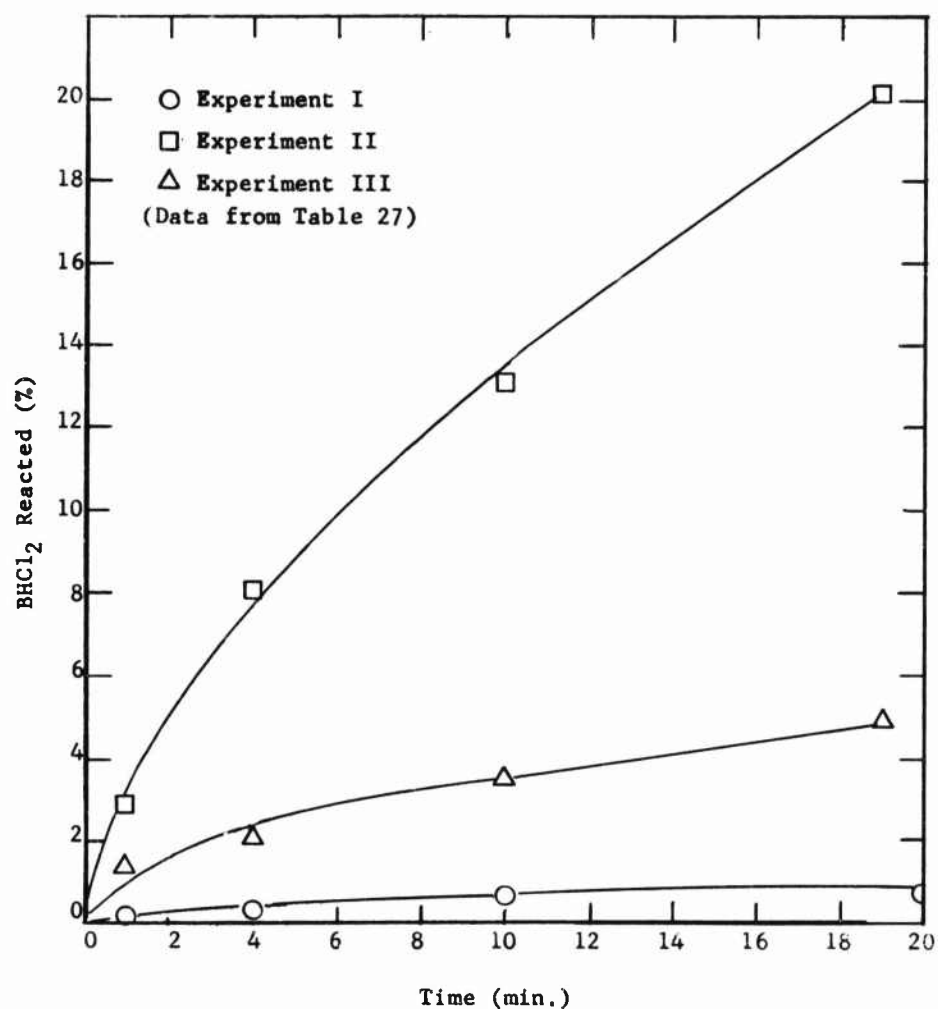


Figure 21. Reaction Rates of Diphenyl Sulfide- BHCl_2 Adduct with Anhydrous HCl at Different Pressures at 0°C

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At 58-60 mm. of HCl the extent of back reaction with a large excess of diphenyl sulfide was less than 4 per cent in 10 minutes of contact time, and less than 1 per cent in 10 minutes with the smaller amount of diphenyl sulfide. When operating at atmospheric pressure the partial pressure of HCl in the reaction will be well below 60 mm., but if the absorption is conducted at higher pressures the partial pressure of the HCl will increase in proportion to the total pressure, and increased rates of back reaction might be encountered. However, contact time during absorption would then have to be minimized.

It was found that the diphenyl sulfide adducts with boron trichloride and dichloroborane are readily soluble in an excess of the diphenyl sulfide, but their solubility in the inert mineral oil "Brillol" was limited. The solubility of the diphenyl sulfide-boron trichloride adduct in Brillol was determined at 0°C. Only 1.4 per cent by weight of the adduct dissolved. It is postulated that this insolubility in the oil helps to repress the back reaction with hydrogen chloride, while on the other hand the solubility of the adduct in excess diphenyl sulfide increases the rate of the back reaction when an excess of the sulfide is used.

Rough measures of solubility in various solvents at ambient temperature were made employing solid diphenyl sulfide adduct which contained both $\phi_2S:BCl_3$ and $\phi_2S:BHCl_2$, although the relative proportion of each was not known. The results are given below:

Solvent	Solubility Gm. $(C_6H_5)_2S$ Adduct/Gm. of Solvent
Toluene	0.89
Cyclohexane	0.37
n-Hexane	0.25
Diphenyl Sulfide	0.14

2. Diphenyl Ether

It has been reported that boron trichloride and diphenyl ether formed a 1:1 complex.⁽¹⁾ A few experiments in the laboratory indicated that it is unlikely that such a complex is formed, based on the vapor pressures of solutions of boron trichloride in diphenyl ether. Because of the high vapor pressure of BCl_3 in diphenyl ether, this system has no merit for separation purposes.

3. Dimethyl Sulfide

Dimethyl sulfide is known to complex with diborane to form $(CH_3)_2S:BH_3$, which is dissociated in the vapor phase to a degree dependent on the temperature. Preliminary work with the dimethyl sulfide-diborane

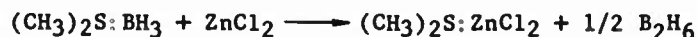
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adduct indicated that recovery of the diborane by fractional distillation would be difficult, possibly because of the rapid reassociation on condensation to the liquid phase. Furthermore, it was found that this adduct reacted rapidly with HCl in the liquid phase according to the following equation:



This system was considered unsuitable, therefore, to recover the reaction gases because of the hydrogen chloride inevitably present.

Recovery of diborane from the dimethyl sulfide adduct was solved, however, by the use of a displacement reaction; that is, zinc chloride was found to displace the diborane as shown in the following equation:



The actual composition of the dimethyl sulfide-zinc chloride complex has not been determined; however, on heating the latter to about 100°C, there is an essentially quantitative recovery of the dimethyl sulfide, which can then be recycled. This process, therefore, would be suitable for recovery of diborane from its mixtures with inert gases, as for example, hydrogen or ethane (gases which commonly accompany diborane in certain types of processing).

It was also observed that boron trichloride also displaced diborane from the dimethyl sulfide, but quantitative recovery of the boron trichloride and dimethyl sulfide could not be obtained by heating the $(\text{CH}_3)_2\text{S}:\text{BCl}_3$ adduct. The boron trichloride was displaced quantitatively from the latter adduct by aluminum chloride, but thermal treatment of the resulting $(\text{CH}_3)_2\text{S}:\text{AlCl}_3$ led to decomposition also.

4. HCl Recovery by Complexing

Hydrogen halides are known to form complexes with certain types of Lewis bases and with aromatic compounds in the presence of suitable Lewis acids. Such complexes may be a means of separating hydrogen chloride from hydrogen (and possibly diborane) without recourse to aqueous solutions. Such a process would eliminate the requirement of drying either the hydrogen chloride or the hydrogen. The following processes were investigated:

s. FeCl_3 -Ether System

Since most ethers split readily in the presence of acids, a stable one was chosen for this purpose; that is, β - β' -dichlorodiethyl ether. It was reported(2) that the following reaction occurs in the FeCl_3 -ether system:

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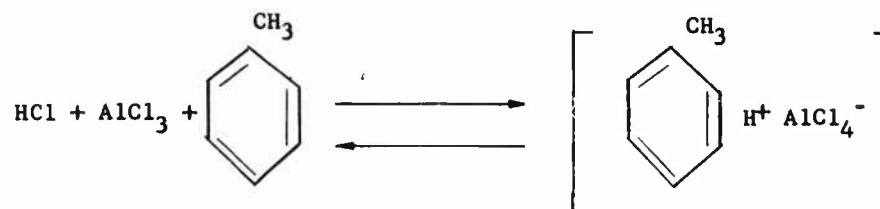


where $\text{R} = (\text{ClCH}_2\text{CH}_2)_2\text{O}$ in the present case. It was found that HCl was absorbed readily and quantitatively by the solution of ferric chloride in β, β' -dichlorodiethylether, and by heating the resulting solution to 100°C , the HCl was completely recovered. When a mixture of diborane and hydrogen chloride was absorbed by the FeCl_3 -dichlorodiethylether solution, the diborane passed through and the hydrogen chloride was retained. During recovery of the hydrogen chloride it was noted that some splitting of the ether had occurred.

Diphenyl ether, used with FeCl_3 , instead of the β, β' -dichlorodiethyl ether, showed only weak complexing ability.

b. Aromatic Compounds

It is known that in the presence of hydrogen halide and a Lewis acid, aromatic compounds, especially alkylated benzenes, behave as bases. It has been shown⁽³⁾ that in the presence of toluene the reaction proceeds as follows:



Below -45°C , one mole of AlCl_3 and one mole of toluene complex one mole of HCl. Above this temperature the complex dissociates to give the pure components.

In the laboratory it was found that m-xylene and mesitylene give stronger complexes than does toluene. However, m-xylene does not reduce the volatility of the HCl sufficiently and the mesitylene complex was so firm that it could not be dissociated without irreversible decomposition.

It is known that hydrogen chloride does not react with BCl_3 in the vapor phase; however, it was found that in the presence of m-xylene a complex corresponding closely to $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{H}^+\text{BCl}_4^-$ was formed at -80°C . This complex appeared to be less stable than its AlCl_3 analogue. It loses hydrogen chloride on evacuation which held at -80°C and, in fact, complete recovery of the HCl can be made by pumping at this temperature.

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c. Dimethyl Sulfide

Aluminum chloride in dimethyl sulfide also formed a stable complex with HCl at room temperature, evidently of the form $(\text{CH}_3)_2\text{SH}^+\text{AlCl}_4^-$. Heating at 100°C under reduced pressure resulted in some irreversible decomposition of the dimethyl sulfide.

d. Copper Sulfate

It is known that copper sulfate forms a complex with hydrogen chloride corresponding to the composition $\text{CuSO}_4 \cdot 2\text{HCl}$. In an initial experiment, 34.7 mmoles anhydrous copper sulfate were treated with a large excess of hydrogen chloride at 760 mm. and ambient temperature in a vessel of large volume. When the pressure reached a constant value the complex was cooled to -80°C and the uncombined hydrogen chloride was pumped off. When the pressure reached about 0 mm., the complex was cut off from the large volume in order to determine its dissociation pressure. At this point the complex was found to contain 63.0 mmoles of hydrogen chloride which gave a composition of $\text{CuSO}_4 : 1.82 \text{ HCl}$. The dissociation pressures on increasing the temperature are as follows:

Temp. (°C)	24.7	35	42	50	60	73	80.5	84	101
Pressure (mm. Hg.)	102	108	113	125	192	336	432	643	847

When these data are plotted, a sharp break is observed at 50°C.

Dissociation pressures were also taken on a complex of composition $\text{CuSO}_4 : 1.07 \text{ HCl}$.

Temp. (°C)	71.5	76	79	81	87
Pressure (mm. Hg.)	122	147	173	226	243

Extrapolation of the latter values to lower temperatures leads to a pressure of about 10 mm. at 25°C and about 1 mm. at 0°C.

The results indicated that the decomposition pressure of the $\text{CuSO}_4\text{-HCl}$ complex is relatively high when two moles of hydrogen chloride are combined with one mole of copper sulfate, but at a $\text{CuSO}_4\text{:HCl}$ mole ratio of 1:1 the pressure is within a range which can be applied for adsorption.

These preliminary results indicated that copper sulfate could be used as an absorbant at a reduced capacity. However, additional experiments revealed that hydrogen chloride was absorbed to only a limited extent by copper sulfate in the presence of liquid boron trichloride.

e. Copper Sulfate-Dimethyl Sulfide

When a mixture of 12.4 mmoles of hydrogen chloride and 12.4 mmoles of dimethyl sulfide was contacted with an excess (34.7 mmoles) of copper sulfate at 29°C, a high rate of absorption was observed, as indicated by the rapid decrease of pressure and evolution of heat.

After the pressure had reached a constant value of about 1 mm., 6 to 7 mmoles of boron trichloride were brought into contact with the brown solid complex, held at 0°C. The pressure of the boron trichloride dropped from an initial pressure of 342 mm. to 95 mm. This observation indicates that boron trichloride is absorbed by the $\text{CuSO}_4\text{-HCl-(CH}_3\text{)}_2\text{S}$ complex and implies that this combination is not suitable in the presence of boron trichloride.

f. Zinc Chloride-Dimethyl Sulfide

Anhydrous zinc chloride did not absorb hydrogen chloride, but in the presence of dimethyl sulfide complex formation was observed. However, it was found to have a relatively high dissociation pressure and methyl mercaptan was formed by splitting of the sulfide. This system was therefore not useful.

D. Absorption in Hexane

Preliminary studies on the partial pressure of boron trichloride dissolved in hexane indicated that it closely followed Raoult's Law. Further experimental work was therefore necessary.

It appeared likely that under appropriate conditions a combination of an inert organic solvent, e.g., hexane, with diphenyl sulfide would be superior as an absorbent to either component alone. The combination would consist of just enough diphenyl sulfide to complex the BHCl_2 plus just enough solvent to absorb the boron trichloride. A comparison of the quantities of absorbent required under various conditions is shown in Table 28. It has been assumed that each component behaves ideally, and that BHCl_2 has a vapor pressure of 1109 mm. at 0°C. It was further assumed that the conversions of BHCl_2 were 20 per cent at a mole ratio $\text{H}_2\text{:BCl}_3 = 3$, and 39 per cent at $\text{H}_2\text{:BCl}_3 = 14$. The data indicate that use of diphenyl sulfide alone or in combination would be advantageous at atmospheric pressure, but that a simple inert solvent such as hexane would be preferable at elevated pressures.

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TABLE 28

Comparison of Absorption Systems^(a)

Pressure	One Atmosphere		Ten Atmospheres	
Mole Ratio H_2/BCl_3	3	14	3	14
Hexane System				
lbs. Hexane/lb. B_2H_6	525	1028	52.5	102.8
Hexane- ϕ_2S System ^(b)				
lbs. Hexane/lb. B_2H_6	160	421	16	42
lbs. ϕ_2S /lb. B_2H_6	40	40	40	40
lbs. Total Absorbent/lb. B_2H_6	200	461	56	82
ϕ_2S System				
lbs. ϕ_2S ^(c)	200	103	200	103

- (a) Absorption at 0°C.
- (b) The hexane serves to dissolve the adduct, but the lesser amounts of hexane will not be adequate to dissolve all of the product. Toluene is a better solvent and might therefore be preferred.
- (c) This assumes one mole equivalent of diphenyl sulfide for every mole of boron used. This would lead to a completely solid adduct and furthermore some of the BCl_3 would escape because of its partial pressure. It would therefore be necessary to employ more diphenyl sulfide than shown to retain all the BCl_3 , and it would require 6 to 7 times the amount shown to hold the adduct in solution.

The effectiveness of a hexane-diphenyl sulfide absorbent was investigated in experiments in which the reaction gases, taken directly from the reactor, were passed countercurrently through either hexane alone or a solution of diphenyl sulfide in hexane. The gases were introduced into the bottom of a column packed with stainless steel Podbielniak Helipak. The liquid absorbent, precooled to 0°C, flowed down from the top of the column at a controlled rate. The actual temperature in the absorption column was between 0°C and 12°C. The results of three representative experiments are shown in Table 29.

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TABLE 29

Countercurrent Absorption Study

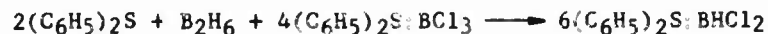
Experiment No.	Conversion Before Absorption (%)	Conversion After Absorption (%)
498-146	22.52	16.8 ^(a)
498-149	24.90	17.3 ^(b)
498-166	23.65	22.75 ^(c)

Absorbent Composition:

- (a) Hexane.
- (b) Hexane containing 7.6% diphenyl sulfide by vol.
- (c) Hexane containing 3.2% diphenyl sulfide by vol.

The considerable amount of back reaction shown in the first two experiments (498-146, 498-149) may be attributable to hydrolysis caused by moisture retained in the absorbent. In the third experiment (498-166), therefore, precautions were taken to dry the absorbent before use and to keep it dry; under these conditions the back reaction in countercurrent absorption seems negligible.

One of the potential difficulties in using a straight liquid absorbent system alone is that disproportionation may take place during the absorption and any diborane formed in the presence of the hydrogen and hydrogen chloride would be difficult to recover. It was considered possible that diphenyl sulfide might catalyze the reaction of diborane with boron trichloride to give a dichloroborane adduct. Therefore, if diphenyl sulfide were incorporated with the organic solvent it might prevent disproportionation. This consideration also leads to the possible use of the combined solvent-diphenyl sulfide system mentioned above. Accordingly, an experiment was conducted to determine if diborane would react with boron trichloride as in the equation:



Into a reaction vessel of calibrated volume, containing 18.50 millimoles of diphenyl sulfide and 137.50 millimoles of hexane, 12.45 millimoles of boron trichloride and 3.15 millimoles of diborane were condensed. The mixture was warmed to 28°C with stirring. The pressure after 12 hours was 201 millimeters. The partial pressure of diborane was estimated to be one millimeter. The solid reaction product suspended in hexane was cooled to

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-78°C and the system was evacuated. Only 0.104 millimoles of diborane were recovered. Thus, 3.05 millimoles of diborane, 12.45 millimoles of boron trichloride and 18.5 millimoles of diphenyl sulfide had reacted, giving the ratio 1.00 diborane to 4.08 boron trichloride to 6.06 diphenyl sulfide in the solid reaction product. This coincides with the requirements of the reaction as given in the equation.

The fact that this reaction took place means that premature disproportionation cannot take place when diphenyl sulfide is used as an absorbent. Furthermore, it is possible to use the diphenyl sulfide-boron trichloride adduct as an absorbing system to recover diborane, even in small quantities, from its admixture with inert gases such as hydrogen; for example, from the pyrolysis step.

E. Absorption in Boron Trichloride

1. Process Description

A number of processes for the separation of the reaction products has been previously discussed. Of the various separation processes, the most feasible appeared to be the absorption-complexing with a mixture of hexane and diphenyl sulfide; however, this involves the introduction of extraneous species into the system. The additional process steps and equipment necessary for the isolation of these species would materially increase the cost of producing diborane.

A substantial simplification could be effected in the process for synthesizing diborane through the use of one of the reactants, boron trichloride, as an absorbent. Details of this simplified process are given below.

The boron trichloride and dichloroborane portions of the cooled reactor effluent are absorbed by a countercurrent flow of liquid boron trichloride in a primary absorption column. The hydrogen chloride and hydrogen are not absorbed and pass out at the absorber as overhead product.

After cooling, the overhead product from the primary absorber is fed in the bottom of a second absorber where the hydrogen chloride is absorbed by a countercurrent flow of very cold boron trichloride, sending relatively pure hydrogen overhead for recycle.

The dichloroborane and boron trichloride from the primary absorber go to a fractionation column where they are separated with consequent disproportionation of the dichloroborane. The bottoms product from the secondary absorber goes to another fractionation column for separation of the hydrogen chloride and boron trichloride.

The required information for engineering design calculations of a pilot plant based on use of boron trichloride as an absorbent was obtained in the National Distillers and Chemical Corporation laboratories.

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2. Solubility of Hydrogen

It was necessary to know the solubility of hydrogen in boron tri-chloride at various temperatures and pressures. Low solubility is preferred, because any hydrogen which dissolves in the boron trichloride finally emerges with the diborane in the disproportionator.

The procedure used to determine the solubilities was the following. Carefully dried hydrogen gas was bubbled slowly through liquid boron tri-chloride at the desired temperature. When the required pressure was reached, the bubbling was stopped and the solution was allowed to stand at the controlled temperature from 4 to 24 hours to insure the establishment of equilibrium. Liquid samples were then withdrawn and vaporized into a large volume, from which samples were taken for mass spectrographic analysis. The results are shown in Table 30 and Figure 22. It is interesting to note that the solubility of hydrogen in boron trichloride increases with temperature, a behavior which is contrary to that of most gases, but not uncommon for hydrogen.

TABLE 30

Solubility of Hydrogen in BCl₃

Temp. (°C)	Part. Press. H ₂ (psia)	H ₂ in Liquid (mole %)			Avg. Liq. Comp. (mole %)
-78	77.7	0.0639;	0.0619;	0.0629	0.0630
-60	64.4	0.1135;	0.1132;	0.1203	0.1156
-60	64.4	0.1125;	0.1140;	0.1076;	0.1106
-60	39.4	0.0719;	0.0766;	0.0660	0.0715
-60	39.4	0.0725;	0.0680;	0.0680	0.0695
-60	14.4	0.0261;	0.0257;	0.0237	0.0252
-30	55.5	0.122;	0.121;	0.119	0.1210
0	85.6	0.275;	0.274;	0.270	0.273
0	55.6	0.187;	0.182;	0.186	0.185
0	30.6	0.0933;	0.0900;	0.0920	0.0918
0	30.6	0.0900;	0.0863;	0.0857	0.0873
24	78.2	0.279;	0.278;	0.280	0.279
24	60.7	0.234;	0.226;	0.223	0.228

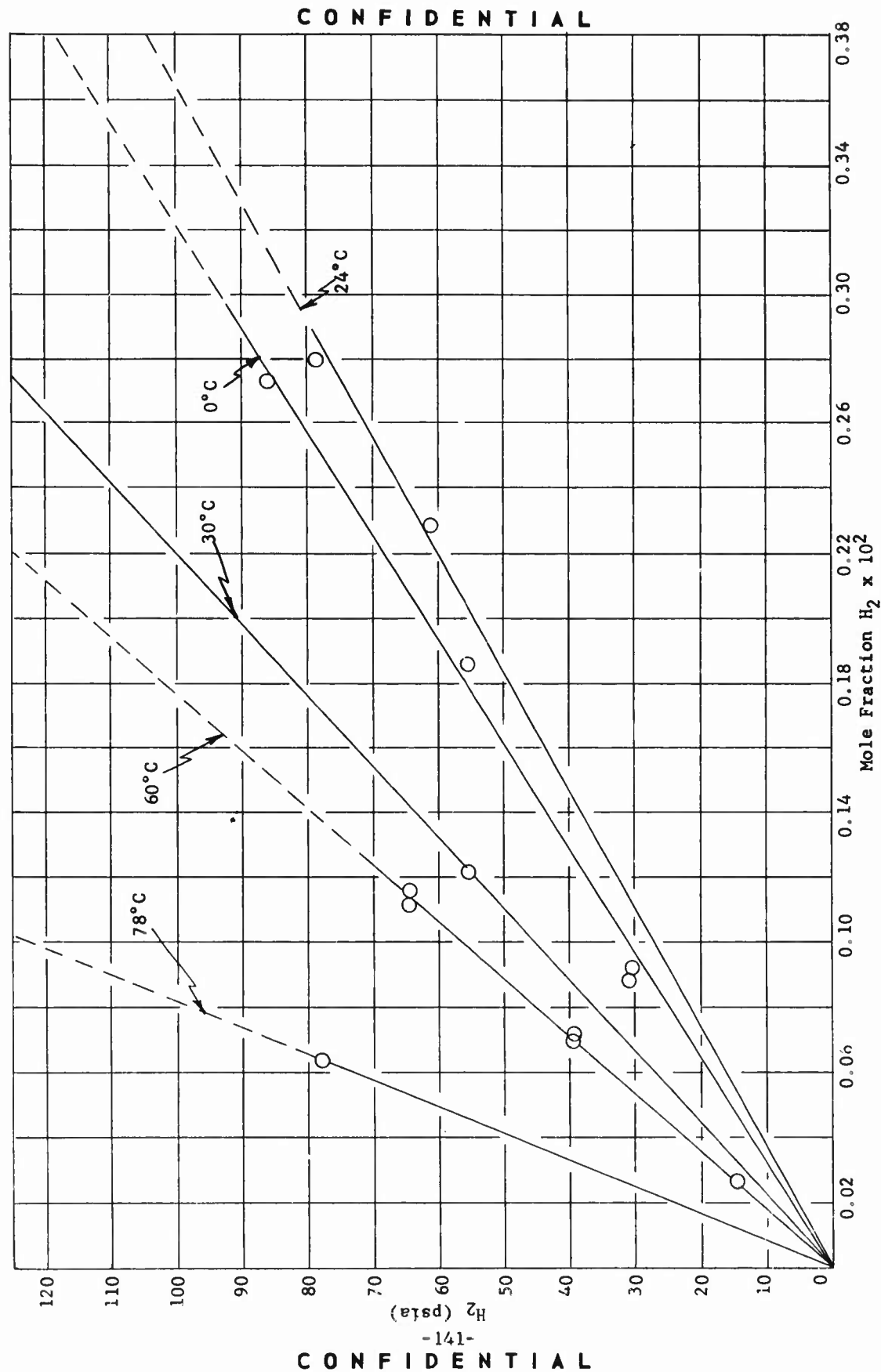


Figure 22. Solubility of H_2 in BCl_3 . Assumes Mole Fraction BCl_3 in Liquid to be 1.0.

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3. Hydrogen Chloride Solubility

The solubility of hydrogen chloride in boron trichloride was determined by measuring the total pressures exerted by solutions of known compositions of hydrogen chloride and boron trichloride at various temperatures.

The apparatus employed in these studies consisted of a 100 ml. round-bottom flask connected to one side of a "Y" shaped mercury manometer, the other side of which was attached to the vacuum system. The bottom side of the manometer was connected to a mercury reservoir to permit raising and lowering of mercury levels in the manometer. The volume of the gas phase in this system was very small compared to that of the liquid phase.

Known amounts of hydrogen chloride and boron trichloride were condensed in the 100 ml. bulb by cooling to liquid nitrogen temperature. The mercury was then introduced into the manometer to seal off the bulb from the vacuum side and the solution was warmed to the desired temperature. One to two hours were allowed for equilibrium, with agitation by tapping of the bulb, until a constant pressure was reached.

From the total pressures and mole fractions of hydrogen chloride, the partial pressures, fugacities and activity coefficients of the hydrogen chloride were calculated. These data, presented in Table 31 and Figure 23, prove that the solubility of hydrogen chloride in boron trichloride is lower than that predicted by Raoult's Law.

TABLE 31

Data on the Solubility of HCl in BCl₃

Amount of BCl₃ = 1155.7 mmoles. Volume of vapor phase = 3-14 cc. depending on the temperature of the liquid phase. The vapor phase was maintained at room temperature.

Temp. (°C)	Mole Fraction X_{HCl}	Total Press. (mm.)	Part. Press. HCl (mm.)	Fugacity F _{HCl} (mm.)	Activity Coeff. γ_{HCl}
0.0	0.01155	810	338	29,300	1.508
0.0	0.01663	954	485	29,150	1.499
-22.6	0.01159	384.2	214.2	18,490	1.849
-22.6	0.01659	475	306	18,450	1.845
-22.6	0.02260	582	414	18,320	1.832
-25.2	0.01157	342	194	16,790	1.840
-25.3	0.01157	346	197	17,070	1.870
-26.1	0.01157	343.5	202	17,500	1.980
-26.3	0.01157	344	204	17,610	1.980
-78.5	0.01161	43	38.5	3,310	3.010
-78.5	0.01663	58	53.5	3,220	2.92
-78.5	0.02265	78	73.6	3,250	2.96

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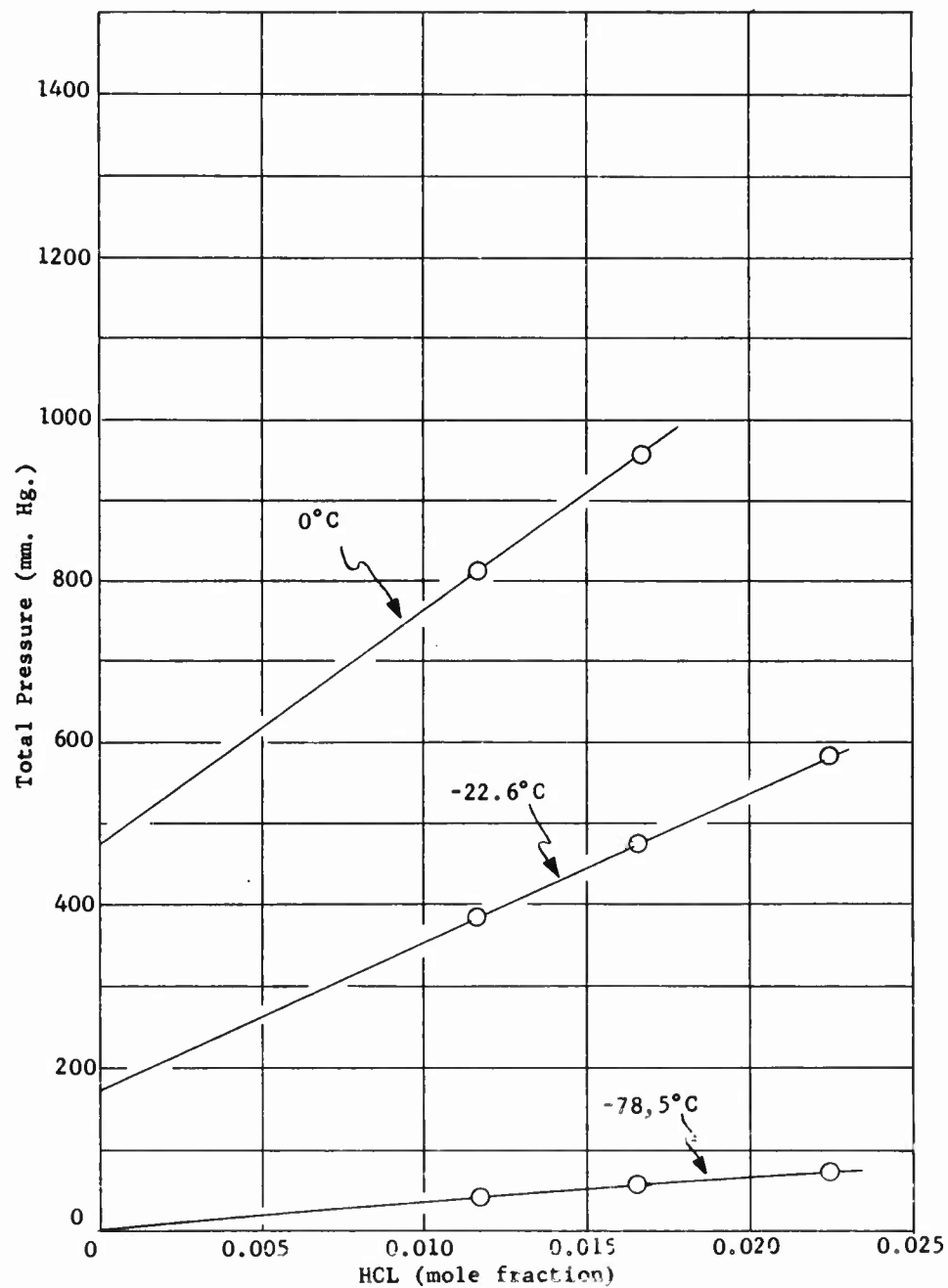


Figure 23. Solubility of HCL in BCl_3

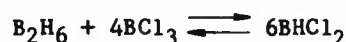
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4. Diborane Solubility

In the same apparatus as was used to study the solubility of hydrogen chloride in boron trichloride, the solubility of diborane in liquid boron trichloride was determined at various temperatures by measurement of the total pressures exerted by solutions of known composition. The results, given in Table 32, were consistent and normal until the last measurement was taken at 0°C. The pressure remained steady at 785.0 mm. for about 1.5 hours, then dropped during the next 23.5 hours to a new steady value of 620 mm. This behavior, confirmed by infrared analysis demonstrating the presence of BHCl_2 , may be explained on the basis of the reaction:



which is apparently greatly accelerated in the presence of liquid boron trichloride. It has been reported elsewhere that diborane and boron trichloride reach equilibrium with BHCl_2 in the gas phase only after 57 days.

TABLE 32

Solubility of Diborane in Liquid BCl_3 ^(a)

Mole Fraction B_2H_6	Temperature (°C)	Observed Total Pressure (mm.)(b)
0.00451	-78.5	15.5
0.00451	-22.9	234.0
0.00451	0.0	578.0
0.00914	-78.5	26.0
0.00914	-22.9	298.0
0.00914	0.0	677.0
0.0141	-78.5	37.0
0.0141	-22.9	364.0
0.0141	0.0	785.0

(a) Conditions:

Total amount of BCl_3 = 1155.7 mmoles.

Total vapor phase = 8-14 ml.

(b) These pressures were recorded after constant values were obtained.

An additional amount of diborane was added to give a mole fraction of 0.0205, and a pressure decrease, which began immediately, was again noted.

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This phenomenon shown in Figure 24 was also observed during work to determine the rate constant for the disproportionation of BHCl_2 in the liquid phase. In a preliminary experiment, 5.09 mmoles diborane and 330.15 mmoles boron trichloride were allowed to stand at 0°C in a glass reactor provided with a mercury manometer. The vapor phase was very small compared with the liquid phase. The initial vapor pressure of 777 mm. Hg. fell, after the lag phase, to 604 mm. during 960 minutes (Curve A, Figure 24). In a second experiment (Curve B), 604.06 mmoles boron trichloride and 5.15 mmoles diborane were stirred at 0°C , and the pressure change followed.

Since these results implied that the reaction is autocatalytic and that BHCl_2 acts as a catalyst to accelerate the reaction, the hypothesis was tested in a third experiment (Curve C) in which BHCl_2 was present from the start. A liquid mixture containing 0.537 mmoles diborane and 23.84 mmoles boron trichloride was allowed to stand in a sealed bulb at room temperature for about 16 hours. This mixture, containing BHCl_2 as shown by infrared, was condensed at -196°C into a mixture of 598.12 mmoles boron trichloride and 5.25 mmoles diborane. The entire mixture was warmed to 0°C and the decrease of pressure with time was recorded.

It is thus apparent from the data that the initial presence of BHCl_2 catalyzed the reaction so that there was no initiation period. Furthermore, the pressure-time curve is "S" shaped, as is characteristic of autocatalytic reactions.

5. Back Reaction in Liquid BCl_3

a. Method A

The apparatus for the study of the back reaction of hydrogen chloride with BHCl_2 (and B_2H_6) in the presence of liquid boron trichloride, as might occur during absorption, was designed so that the gas phase, contained in a two-liter vessel, could be bubbled continuously through the relatively small liquid phase by means of a diaphragm pump. Outlets were provided to permit withdrawal of liquid or gas phase samples as desired. Pressure was measured by a Bourdon gauge. The use of a large gas volume relative to liquid volume was necessary in this static method to maintain a relatively constant partial pressure of hydrogen chloride during the back reaction.

A mixture containing B_2H_6 , BHCl_2 and BCl_3 was introduced into this system and the gas phase was bubbled through the liquid phase for a period of time to permit equilibrium to be attained. The mixture employed was the same that had been employed in the previous experiments on the solubility of diborane in boron trichloride. It was transferred to the apparatus by distillation under vacuum. The liquid phase was then brought to 0°C and the gas phase remained at ambient temperature. The

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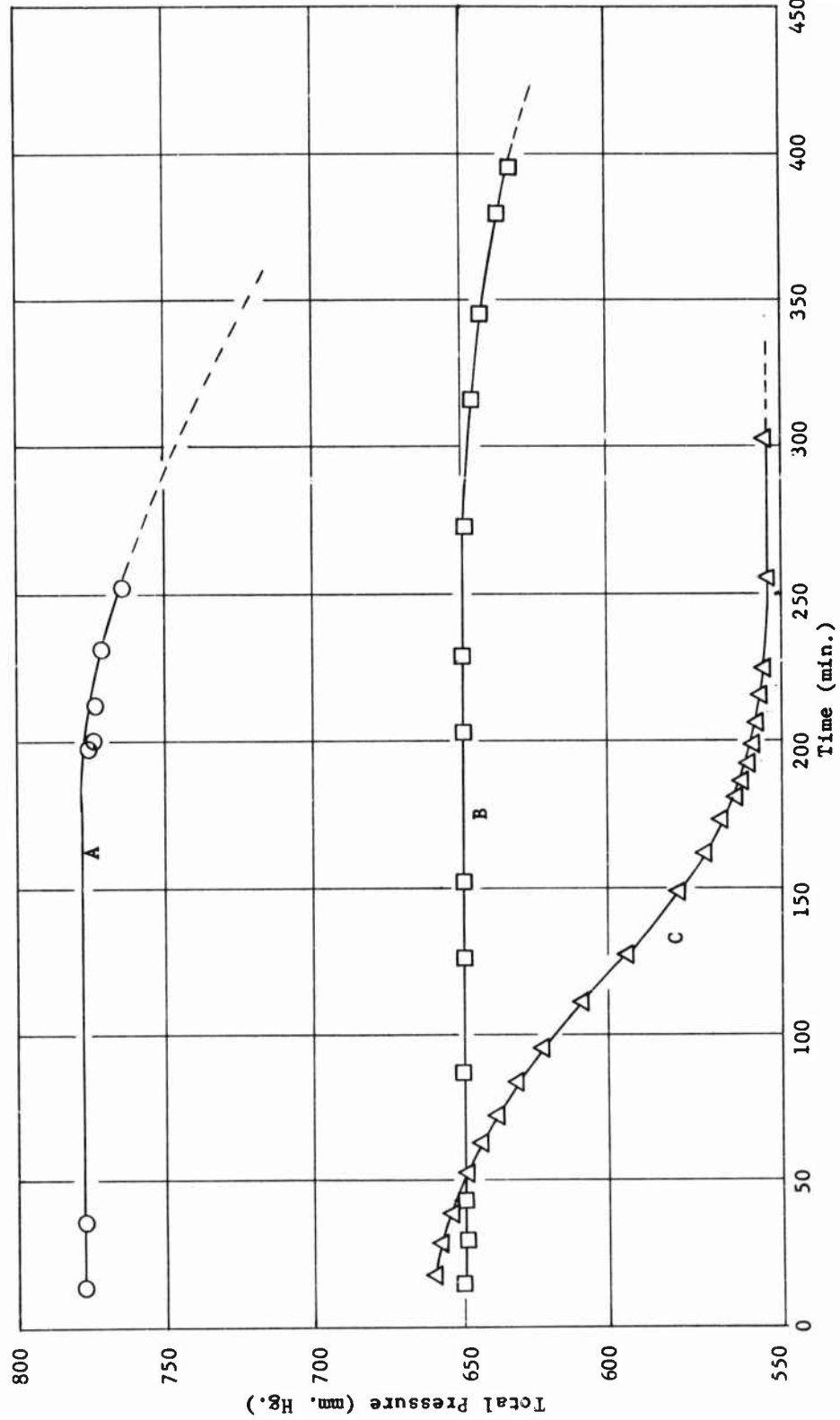


Figure 24. Rate of Hydrogen Chlorine Exchange Between B_2H_6 and BCl_3 in Liquid BCl_3 at $0^\circ C$

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TABLE 33

	Composition of Vapor	
	After 8 hrs. (mole %)	After 10 hrs. (mole %)
BCl ₃	71.3	71.6
BHCl ₂	13.87	14.0
B ₂ H ₆ (by diff.)	14.83	14.4

Init. total charge of BCl_3 = 1155.7 mmoles;
of B_2H_6 = 23.6 mmoles.
Total vol. of apparatus = 2105.0 ml.
Est. liquid phase vol. = 94.0 ml.
Total pressure = 633 mm.
Total gas in vapor phase = 71.1 mmoles

TABLE 34

	Fugacities at 0°C	
	F _B Cl ₃ (mm.)	F _B HCl ₂ (atm.)
Data after 8 hours	481	1.900
Data after 10 hours	484	1.860
Literature	477	
Calculated from other data		1.827

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analysis. After four more hours of pumping, samples were again withdrawn. The following shows the results:

	Composition, Mole % After 7 Hrs.		Composition, Mole % After 11 Hrs.
	Liquid Phase (by hydrolysis)	Vapor Phase (infrared)	Vapor Phase (infrared)
BCl ₃	95.0	81.6	83.6
BHCl ₂	5.0	13.3	12.5
B ₂ H ₆	-	5.1	3.9
		(by diff.)	(by diff.)

The difference in analysis of the vapor phase after 7 hours and after 11 hours could be an indication that equilibrium had not yet been reached after 7 hours. However, a decrease in diborane should be accompanied by an increase in BHCl₂ and a decrease in BCl₃, which is contrary to the analytical data. Part of the difficulty is probably connected with an inherent limit in the accuracy of the analytical method (especially diborane when determined by difference). When equilibrium seemed to be assured, hydrogen chloride was added and the rate of change in concentration of the BHCl₂ was determined.

The gas phase was continually pumped through the liquid, and liquid and vapor phase samples taken at measured intervals for analysis.

The results showed an erratic trend in the decrease of hydride content, however, and it was decided that in this system it was not possible to maintain equilibrium conditions adequately to obtain accurate measures of reaction rates. Consequently another method of measuring the rate of back reaction was devised, as described under Method B.

b. Method B

Although the back reaction, $\text{BHCl}_2 + \text{HCl} \longrightarrow \text{H}_2 + \text{BCl}_3$, shows no change in the number of moles of gas as the reaction proceeds, it should be possible to measure an increase in pressure because of the fact that hydrogen is much less soluble in boron trichloride than is the hydrogen chloride.

The reaction was carried out in a stainless steel pressure vessel provided with a Bourdon gauge, and in which the vapor volume was kept small compared to the liquid volume. The reaction vessel was charged with 682.76 mmoles of boron trichloride and 3.17 mmoles of diborane and agitated for three days at ambient temperature to permit the BCl₃-BHCl₂-B₂H₆ equilibrium to be established. In another pressure vessel connected to the reaction vessel, but closed off by a valve, were contained 6.28 mmoles of hydrogen chloride and 289.66 mmoles of boron trichloride. After equilibrium conditions had been reached in the reaction vessel, it was immersed in an ice bath and with constant shaking given time to reach 0°C.

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Now the $\text{BCl}_3\text{-HCl}$ solution (at about 7°C) was permitted to run as a liquid into the reaction vessel by opening the connecting valve for a short time. Measurement of the hydrogen chloride and boron trichloride which had not entered the reaction vessel showed that 5.04 mmoles of hydrogen chloride and 261.35 mmoles of boron trichloride had gone into the reactor. Following are the over-all mole fractions of materials in the reactor:

	<u>Mmoles</u>	<u>Mole-Fraction</u>
BCl_3	931.43	0.097482
HCl	5.04	0.00527
BHC1_2	<u>19.02</u>	0.01991
	955.49	

The increase of pressure with time was noted and is recorded in Table 35 and plotted in Figure 25.

TABLE 35

Back Reaction of HCl with BHC1_2 ^(a)

Time (min.)	Pressure (psia)	Time (min.)	Pressure (psia)
Before HCl addn.	13.6	376	23.7
0	18.7	456	25.2
After HCl addn.			
2.25	18.6	506	25.8
3.25	18.7	569	26.7
4.25	18.7	625	27.0
9.25	18.7	2059	35.8
47	18.7	2225	37.8
77	19.7	2466	39.7
106	19.7	2621	41.7
136	20.2	2866	43.7
166	20.7	2926	44.7
197	21.2	3468	48.9
226	21.7	3730	51.1
257	21.8	3993	53.2
294	22.5	4233	55.2
317	22.8	4942	59.0

(a) Conditions:

Vol. of liquid phase = 81.1 ml.
Vol. of gas phase = 23.4 ml.
Temp. of reaction = $0^\circ\text{C} \pm 1^\circ\text{C}$.

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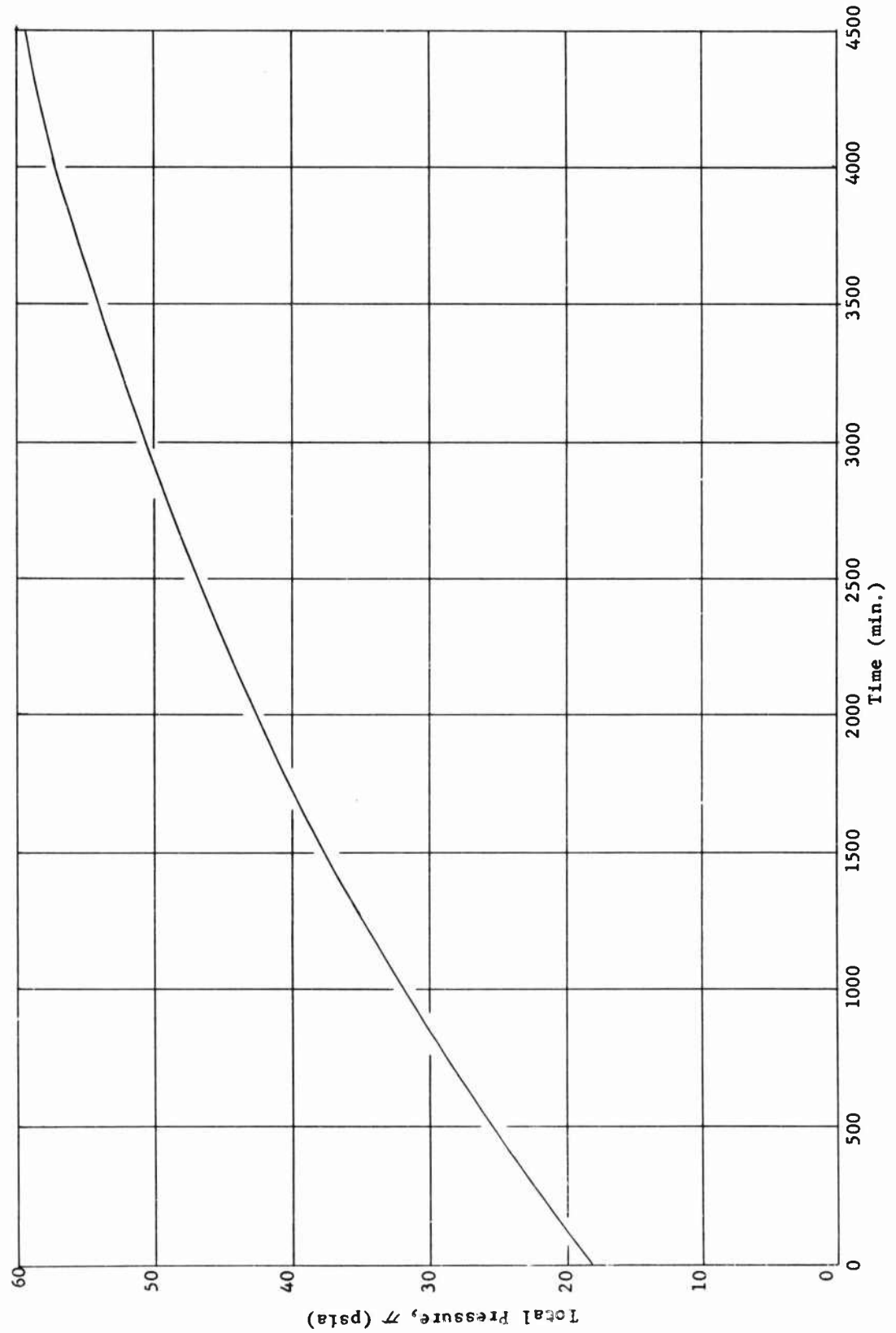


Figure 25. Total Pressure of Reaction Vessel at 0°C

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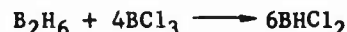
A sample of the liquid was withdrawn at the end of the reaction and a wet analysis performed.

Examination of the data shows that the back reaction follows first order kinetics with respect to both BHCl_2 and HCl , according to the equation:

$$\frac{dx}{d\theta} = kx_{\text{BHCl}_2} \cdot x_{\text{HCl}}$$

where x is the mole-fraction of each reactant. The rate constant, k , was found to be 0.018 min.^{-1} at 0°C .

Further experiments were designed to confirm the order of reaction with respect to BHCl_2 by operating with a large excess of HCl over BHCl_2 . In these experiments, the BHCl_2 was prepared by the interaction of B_2H_6 and BCl_3 , according to the equation:



In a typical experiment, at 0°C , a liquid mixture of 1296.13 mmoles of BCl_3 and 2.89 mmoles B_2H_6 was allowed to stand at room temperature in a stainless steel reactor with very small vapor space to produce BHCl_2 . After five to six days the vapor phase was examined by infrared and was observed to consist entirely of BHCl_2 and BCl_3 ; there was no detectable B_2H_6 . After the mixture had equilibrated at 0°C , a liquid mixture of 185.83 mmoles HCl and 249.11 mmoles of BCl_3 was added. Continuous agitation was applied and the pressure rise with time was followed. The rate constant was found to be 0.030 min.^{-1} compared to the value of 0.018 min.^{-1} obtained in the first experiment described. It is believed that the high k value is the more accurate.

This procedure was employed to determine the value of the rate constant at 24.5°C and 37.0°C with all results tabulated as follows:

Temp. ($^\circ\text{C}$)	k (min.^{-1})
0	0.018
0	0.030
24.5	0.098
37.0	0.092

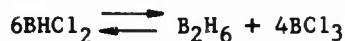
The values obtained give a reasonable measure of the rate of reaction, but are not sufficiently accurate to give a reliable Arrhenius plot for determination of the activation energy.

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IV. Disproportionation

A. Rate

Experiments were conducted to determine the extent and rate of disproportionation according to the equation:



The method used was simply to reflux a solution of BCl_3 and BHCl_2 and to collect the non-condensable gas (B_2H_6) emanating from the top of the reflux condenser. These runs were conducted at atmospheric pressure and the reflux condenser was cooled to -78°C with dry ice. The B_2H_6 was collected in a trap, cooled by liquid N_2 , following the reflux condenser. In one experiment a fractionating column filled with Podbielniak stainless steel Helipaks was interposed between the boiling flask and the reflux condenser. In the other experiments no fractionating column was used. Results are given in Table 36.

TABLE 36

Disproportionation of BHCl_2

Expt. No.	Distillate Fraction No.	Time of Reflux (min.)	Average Pot Temp. ($^\circ\text{C}$)	Boiling Rate (drops/min.)	Contents of Collector (mmoles)		
					H	B	Cl
486-150(a)	1	210	-	-	36.90		
	2	225	-	-	2.70		
	3	120	-	-	0.60		
	Totals	555			40.20		
486-157(b)	1	30	11.6	228	23.86	8.29	3.63
	2	30	12.8	265	4.02	1.40	0.11
	3	60	13.0	280	2.90	0.96	0.10
	4	90	13.2	266	4.60	1.60	0.21
	Totals	210			35.38	12.25	4.05
486-166(c)	1	5	11.8	-	19.99	9.39	11.31
	2	10	12.6	288	1.03	0.38	0.10
	3	30	13.4	299	3.67	1.26	0.10
	4	60	14.6	265	2.78	0.98	0.13
	5	63	14.9	256	1.71	0.63	0.10
	Totals	168			29.18	12.64	11.74

- (a) Initial Charge: 245.56 mmoles BCl_3 .
40.52 mmoles BHCl_2 .
(b) Initial Charge: 113.32 mmoles BCl_3 .
36.94 mmoles BHCl_2 .
(c) Initial Charge: 76.16 mmoles BCl_3 .
30.48 mmoles BHCl_2 .
3.09 mmoles HCl .

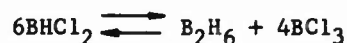
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The recoveries of total available diborane were 99.3 per cent in 9.3 hours, 95.8 per cent in 3.5 hours, and 95.7 per cent in 2.8 hours, respectively. The major portion of the diborane was collected very rapidly and presumably the recoveries of the latter two experiments would have been higher if they had been continued longer. The observed H/B ratio was, in general, below the theoretical value of 3.0; this is attributed to the small amounts of BCl_3 and BHCl_2 carried over into the collector by the gases leaving the reflux condenser at -78°C .

B. Equilibrium Constant

The value of K_x for the reaction



was redetermined in the course of studying the back reaction in liquid BCl_3 . The four experimental values obtained at 0°C were:

$$K_x = \frac{(x_{\text{B}_2\text{H}_6})(x_{\text{BCl}_3})^4}{(x_{\text{BHCl}_2})^6}$$

<u>Expt. No.</u>	<u>K_x</u>
486-274	13.1×10^3
486-276	7.28×10^3
654-50	12.9×10^3
654-59	52.5×10^3
Best Value	15.93×10^3 (geometric mean)
$\text{Log}_{10} K_x$	$= 4.203 \pm 0.259$ (avg. dev.)

It was possible to combine this result with fugacity data to derive a value of K_p (gas phase equilibrium constant). The following values of the fugacity have been used:

$$F_{\text{BCl}_3} = 0.628 \text{ atm. (literature value)}$$

$$F_{\text{BHCl}_2} = 1.880 \pm 0.020 \text{ atm.}$$

$$F_{\text{B}_2\text{H}_6} = 29.6 \text{ atm.}$$

$$K_p = K_x \frac{(F_{\text{B}_2\text{H}_6})(F_{\text{BCl}_3})^4}{(F_{\text{BHCl}_2})^6} = 0.1660 \text{ atm.}^{-1} \text{ at } 0^\circ\text{C} \text{ or } 2.18 (\text{mm. Hg.})^{-1}$$

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C. The Reaction of HCl with B₂H₆

Since an imperfect separation process would lead to HCl contamination of the B₂H₆ produced, it was important to learn if HCl reacts with B₂H₆. If a reaction does occur, it may be possible to purify HCl contaminated B₂H₆ under conditions which promote the reaction.

An experiment was designed so that the reaction of HCl with B₂H₆ in the gas phase over a period of time could be followed by infrared analysis. A mixture of 12.09 mmoles of HCl and 12.02 mmoles of B₂H₆ were condensed into the vessel and then permitted to reach room temperature. Infrared analyses at various intervals are shown below:

	Mole % After 105 min.	Mole % After 225 min.	Mole % After 21.75 hrs.
B ₂ H ₆	45.3	45.6	35.3
BHCl ₂	1.05	3.33	7.67
BCl ₃	-	3.95	10.5

It was also noted after 225 minutes that bands at 11.8 μ and 12.05 μ were appearing. These bands correspond to the bands reported by Aerojet-General for B₂H₅Cl.

In all measurements of BHCl₂ no correction was made for the effect of B₂H₅Cl on the band at 9.1 μ . Non-condensable gas (H₂) was observed during the manipulation of the samples for infrared analysis.

A mixture was prepared containing less hydrogen chloride; that is, 22.72 mmoles diborane and 4.34 mmoles hydrogen chloride, and the mixture was also examined by infrared, as follows:

	Mole % After 55 min.	Mole % After 19.5 hrs.
B ₂ H ₆	77.4	78.3
BHCl ₂	0.469	3.34
B ₂ H ₅ Cl	Very Small	Small

A mixture containing 19.59 mmoles diborane and 0.362 mmoles hydrogen chloride gave the following results:

	Mole % After 60 min.	Mole % After 145 min.	Mole % After 21.5 hrs.
B ₂ H ₆	94.6	99.3	94.1
BHCl ₂	None	0.289	0.336
B ₂ H ₅ Cl	None	Trace	Trace

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It is evident, therefore, that B_2H_6 reacts with HCl at an appreciable rate to produce $BHCl_2$, BCl_3 , B_2H_5Cl and H_2 . The conditions under which these reactions were conducted were much milder than those to be employed in the pilot plant where much higher temperatures and pressures are used and which should increase the rate of back reaction accordingly. If HCl appears with B_2H_6 in the disproportionator, where the hold-up time is very high compared to the hold-up in, say, the primary absorber, a considerable amount of back reaction may take place.

The relative volatility of HCl with respect to $BHCl_2$ is very high compared to relative volatility of HCl versus B_2H_6 and it is clearly most logical to effect complete separation of the HCl before the reaction product reaches the disproportionator. The back reaction which can take place in the disproportionator, as well as in any purifying unit following the disproportionator, makes the logic of effecting the separation prior to the disproportionator even more compelling.

V. Properties of Boron Compounds

A. Physical Properties of BCl_3

The following empirical formulae⁽⁴⁾ for the physical properties of BCl_3 over a temperature range of $-40^\circ C$ to $\pm 10^\circ C$ for one atmosphere are quoted:

1. Density of the liquid:

$$\rho_L (\text{gm./cc.}) = 1.3730 - 0.002159 t(^{\circ}C) - 8.377 \times 10^{-7} t^2$$

2. Viscosity of the liquid:

$$\mu_L (\text{c.p.}) = \frac{0.3442}{1 + 0.006966t - 5.9013 \times 10^{-6} t^2}$$

3. Thermal conductivity of the liquid:

$$K_L (\text{cal./sec.-cm.-}^{\circ}C) = 25.88 - 0.0525t$$

Mellor reports two values of the liquid density.⁽⁵⁾ Another value is given by Stauffer Chemical Company.⁽⁶⁾ These are not in agreement with the above data.

Three methods of estimating viscosities from structural considerations are obtained.⁽⁷⁾ By using viscosity data for diborane⁽⁸⁾ the structural values of boron were established and estimates made for boron trichloride. These agreed best with data of (2) above. All data are plotted in Appendix C.

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B. Boiling Points

Experimental determinations of the vapor pressure of pure BHCl_2 have been obscured by the instability of the pure compound at ordinary temperatures. There appeared to be reason to doubt the validity of estimates based on analogy to compounds of other elements. One of the more successful empirical methods of estimation has been based on the parachor of Sugden. Where a compound may be viewed as a member of an homologous series, the boiling point of each member will generally be a regular function of the parachor. Where there is little change in polarity from member to member, the curvature of this function is small and extrapolation may be accurate.

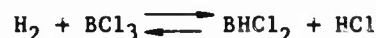
The compound BHCl_2 may be regarded as a member of many individual homologous series such as BHX_2 , BCl_2 , $\text{BH}_n\text{Cl}_{3-n}$, $\text{R} = \text{CH}_3$, $\text{R} = \text{C}_2\text{H}_5$, etc. For each such "family", a single, smooth plot of parachor versus boiling point can be constructed. Owing to a lack of complete data in the literature, not all these primary data could be obtained directly.

The available literature data are listed in Appendix D together with the plot of parachor versus boiling point for each homologous series. The values used for the parachors are taken from previous National Distillers Chemical Corporation laboratory work and from Hougen and Watson.⁽⁹⁾

On the basis of these data, it is estimated that the boiling point of BHCl_2 is $-13^\circ\text{C} \pm 4^\circ\text{C}$ at 760 mm.

VI. Thermodynamic Data

A confidential report⁽¹⁰⁾ has presented accurate data for the equilibrium constant of the reaction:



$$K = \frac{P_{\text{BHCl}_2}}{P_{\text{H}_2}} \times \frac{P_{\text{HCl}}}{P_{\text{BCl}_3}}$$

at temperatures of 300°C to 1000°C . A previously used confidential report⁽¹¹⁾ presented a value for the equilibrium constant of the reaction:

$$6\text{BHCl}_2 = \text{B}_2\text{H}_6 + 4\text{BCl}_3$$

$$K_p = \frac{P_{\text{B}_2\text{H}_6} \times P_{\text{BCl}_3}^4}{P_{\text{BHCl}_2}^6} = 0.7 \pm 0.3 \text{ mm.}^{-1}$$

at 25°C . From this, the value of K at 25°C may be accurately computed as:

$$K = 0.947 \times 10^{-9} \pm 0.01 \times 10^{-9}$$

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The best fit (visual, not least squares) of these data was obtained by the equation:

$$\log_{10} K = 1.521 - 0.3694 \left(\frac{10^4}{T}\right) + 0.0016432 \left(\frac{10^4}{T}\right)^2$$

From this it is possible to derive several valuable sets of data:

1. Heat of reaction for the hydrogenation

$$\begin{aligned} \Delta H^\circ &= \frac{d}{d(1/T)} (R \ln K) \\ &= 4.5760 \times 10^4 \left[-0.3694 + 0.0032864 \left(\frac{10^4}{T}\right) \right] (\text{cal/mole}) \end{aligned}$$

2. $\Delta C_{p, \circ}$ of the hydrogenation

$$\begin{aligned} \Delta C_{p, \circ} &= c.p.(BHC1_2) + c.p.(HCl) - c.p.(H_2) - c.p.(BCl_3) \\ &= \frac{d(\Delta H^\circ)}{dT} = + \frac{1,503,874}{T^2} (\text{cal/mole} - ^\circ K) \end{aligned}$$

Since $\Delta C_{p, \circ}$ is the second derivative of the original data, the accuracy of this figure is apt to be poor.

3. Heat of formation of $BHC1_2$ at various temperatures

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(BHC1_2) + \Delta H_f^\circ(HCl) - \Delta H_f^\circ(H_2) - \Delta H_f^\circ(BCl_3) \\ &= 4.5760 \times 10^4 \left[-0.3694 + 0.0032864 \left(\frac{10^4}{T}\right) \right] (\text{cal/mole}) \end{aligned}$$

By use of the values of the heats of formation at various temperatures as given in the Bureau of Standards Circular 500, the heat of formation of $BHC1_2$ was computed at 278°K to 500°K.

4. Free energy of formation and absolute entropy of $BHC1_2$ at 298°K

a. When the value of K_p at 25°C as stated above and the NBS values for the free energy formation of BCl_3 and B_2H_6 are used, the free energy of formation of $BHC1_2$ at 298°K is found to be -58,423 cal/mole.

b. For the hydrogenation reaction:

$$\frac{d(-RT \ln K)}{dT} = -\Delta S^\circ$$

then

$$\Delta S^\circ = 4.576 \left[1.52 - 0.0032864 \left(\frac{10^4}{T}\right)^2 \right] (\text{cal/mole} - ^\circ K)$$

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The value of ΔS° at 298°K is found to be -9.97 cal/mole-°K. Using NBS values of absolute entropy for H_2 , BCl_3 and HCl , the value of S for $BHCl_2$ at 298°K is found to be + 45.91 cal/mole-°K.

5. Equilibrium constant for the disproportionation (K_p)

At any temperature, the relation between the disproportionation equilibrium constant (K_p) and that of the hydrogenation is expressed by:

$$-RT \ln(K \times K_p^{1/6}) = \Delta F^\circ_f(HCl) + 1/6 \Delta F^\circ_f(B_2H_6) - 1/3 \Delta F^\circ_f(BCl_3)$$

where:

$$\Delta F^\circ_f(N) = \text{standard free energy of formation of compound N.}$$

Using the NBS values for the free energies of formation on HCl , B_2H_6 and BCl_3 , the value of K_p was estimated from 278°K to 500°K.

6. Heat of reaction, ΔH° , for the disproportionation

On use of the heat of formation of $BHCl_2$ computed in (3) above and the NBS values of the heats of formation of BCl_3 and B_2H_6 , the heat of reaction for the disproportionation was computed by the relation:

$$\Delta H^\circ = \Delta H^\circ_f(B_2H_6) + 4 \Delta H^\circ_f(BCl_3) - 6 \Delta H^\circ_f(BHCl_2)$$

for temperatures between 278°K and 500°K.

Detailed plots of these data appear in Appendix E.

VII. Analytical Methods

In general, no methods of analysis were developed which could be considered entirely satisfactory. Chemical analysis was the most reliable, but it was slow and did not distinguish between B_2H_6 and $BHCl_2$. Furthermore, determination of the amount of HCl present was based on a calculation of differences which could easily magnify a small percentage error to a large one.

A. Chemical Methods

The procedure employed for chemical analysis involved first the condensation of the products into a vessel containing water frozen at -196°C, sealing the vessel, and then allowing the water and products to warm up. The hydrolysis products consisted of boric acid, hydrochloric acid and hydrogen. The hydrogen was isolated by means of a Toepler pump and measured. The total boron and hydrochloric acid were determined titrimetrically. From these data, the boron hydride content was found

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and the conversion and yield could be calculated based on the boron and chlorine balance.

As already indicated, the chemical method did not distinguish between B_2H_6 and $BHCl_2$, although it did reveal the total number of B-H bonds formed. The amount of HCl formed could be calculated also, but because it involved a calculation by differences, a small experimental error could be magnified considerably.

B. Instrumental Methods

1. Infrared Spectroscopy

The use of infrared should be ideal for analysis of these materials because distinct absorption bands specific for each component present can be observed. Unfortunately, pressure broadening effects to a significant degree were observed with these materials; that is, the presence of each component affected the absorption curves of the other components present. Consequently, to obtain reliable results it was necessary to set up a series of calibration curves which delineated the mutually interacting effects.

An infrared calibration curve of $BHCl_2$ in the presence of BCl_3 was prepared. A mixture of $BHCl_2$ and BCl_3 of known hydride content (as determined by the hydrolysis) was used in the determination of the optical densities of $BHCl_2$ at various total pressures. Knowing the partial pressures of BCl_3 , the differences from total pressures were considered those of $BHCl_2$. From these data the optical densities of $BHCl_2$ were determined and the extinction coefficients calculated. For a one cm. cell at $25^\circ C$ with sodium chloride windows and with double slits, the following values were obtained:

	<u>Wavelength</u>	<u>Extinction Coefficient (k)</u>
BCl_3	10.10μ	1.9×10^{-2}
$BHCl_2$	9.12μ	1.2×10^{-2}

The optical density of $BHCl_2$ was linear with respect to its partial pressure up to 6 mm. The partial pressures of BCl_3 in the mixtures were adjusted not to exceed 45 mm. A one cm. cell was employed for this work because the absorption of BCl_3 was too strong in a larger cell, unless very low pressures were used.

American Potash & Chemical Corporation reported similar calibration curves for $BHCl_2$ using 3.9μ and 9.12μ bands. Since separate calibrations were required for different machines, it was necessary in any case to determine such a calibration curve independently. The 3.9μ curve would not be useful in the presence of appreciable amounts of B_2H_6 since the latter also absorbed in that region. Following is a comparison

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of extinction coefficients determined by American Potash & Chemical Corporation and National Distillers Chemical Corporation:

	Wavelength	<u>Extinction Coefficient</u>	
		AP&CC	NDCC
BCl ₃	10.1 μ	1.5×10^{-2}	1.9×10^{-2}
BHCl ₂	9.12 μ	2.1×10^{-2}	1.2×10^{-2}
BHCl ₂	3.9 μ	1.6×10^{-3}	1.7×10^{-3}

Diborane cannot be measured in the one cm. cell and it was therefore not possible to determine its effect on the BHCl₂ calibration curve.

Further studies on infrared spectra have shown the following:

- a. Hydrogen has no pressure broadening effect on BHCl₂ in the 9.12 μ band nor on BCl₃ at the 10.1 μ band.
- b. Hydrogen chloride has no pressure broadening effect on BHCl₂ at 9.12 μ nor on BCl₃ at 10.1 μ .

Infrared analysis of known mixtures of BCl₃ and B₂H₆ showed that B₂H₆ can be measured accurately (using the 2.8 μ band) in the partial pressure range of 10 mm. to 120 mm. in the presence of BCl₃. The latter exerts no pressure broadening effect on B₂H₆. Within the same range of pressures there has been observed a scatter of points with respect to the determination of BCl₃ in the presence of B₂H₆. Apparently there is no specific pressure broadening effect. When pure BCl₃ is put into the IR cell it is found on standing that the band of 8.3 microns increases in intensity with time. This effect has been produced rapidly by the addition of a slight amount of water, and accordingly it is attributed to a species, such as BCl₂(OH), Cl₂BOBCl₂ or Cl₃O₃B₃, which might result from hydrolysis. It is considered that the scatter of points which appears when B₂H₆ is present may be due to this effect, it being assumed that during the process of introducing the B₂H₆ sample the extra manipulations and extra time permit a greater effect of trace moisture. The bands at 7.05 microns (preferred) and 6.85 microns are employed for the determination of BCl₃ in the presence of B₂H₆, but they are also affected to a slight extent when the band at 7.3 microns increases.

2. Vapor Phase Chromatography

The determination of boron hydrides by vapor phase chromatography has been well developed and procedures are described in the literature. However, it has been found that mixtures which include BCl₃ and BHCl₂ are a special problem. The usual supporting materials, such as fire brick, tend to retain the boron trichloride. Capillary columns or

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stainless steel packed columns wetted with an inert oil or with diphenyl sulfide gave considerable tailing.

The mass spectrograph gave fairly reliable results with a mixture of BCl_3 and B_2H_6 . However, it was difficult to eliminate traces of moisture in the mass spectrograph and moisture sensitive materials were thereby affected.

3. Electrical Conductivity of HCl in Liquid BCl_3

Since it would be convenient for plant control purposes to determine the concentration of HCl in liquid BCl_3 by measurement of the specific resistance, a conductivity cell was installed in the high vacuum system, and solutions of HCl in BCl_3 were prepared with various partial pressures of HCl . At total pressures up to 577 mm. Hg. (liquid at 0°C), the specific resistance was beyond the scale limit (250×10^6 ohms-cm.) of the instrument used (Industrial Instruments, Inc. Conductivity Bridge Model RC-16B-1, cell constant 0.1). Since sensitivity at low concentrations is desired, it might be possible to increase the cell sensitivity by reducing the distance between the electrodes and by use of larger electrode areas.

PREPILOT PLANT EVALUATION

I. Reactor Development

The first objective of this program was to obtain specific information regarding suitable materials of construction, configuration, and operating conditions which would permit design of the pilot plant hydrogenation reactor. The first of these was particularly important since data on the relationships of operating conditions to conversions and yields were being accumulated in the laboratories of National Distillers and Chemical Corporation.

A. Equipment

1. General Arrangement

The schematic flowsheet of equipment to study the hydrogenation of BCl_3 is shown in Figure 26. This general equipment arrangement was used during Runs 100 through 602.

Hydrogen gas from pressurized cylinders passed in succession through a pressure regulator, an orifice-type flowmeter, a hot copper deoxidizer, a cooler-condenser, and a silica gel drying tube before entering the hydrogen preheating coil.

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Boron trichloride liquid was forced by pressure through a porous Teflon filter, an orifice type flowmeter, and a flow regulating valve before entering the boron trichloride vaporizing and preheating coil.

The exact arrangement of boron trichloride and hydrogen preheating systems was varied during this portion of the program. The particular preheater arrangement shown in Figure 26 was that used in Run 208.

From the reactor the gas products passed through a cooling coil, immersed in water, thence to a porous porcelain filter, and then through a flow regulating valve before being discharged to the scrubbing and clean-up towers for disposal.

Product gas samples collected in the sample storage chamber were transferred to the glass vacuum system for sample manipulation and analysis.

2. Hydrogenation Reactors

Details of the hydrogenation reactors are summarized in Table 37. The design of the first hydrogenation reactor which was tested is shown in Figure 27. The first reactor of this design was made of carbon steel, and the second of stainless steel, Type 347. Reactants, hydrogen and boron trichloride, were premixed in the head of the reactor before passing into the reaction chamber.

The next reaction chambers are detailed in Figures 28 and 29. The revised reactor head design for these reactors permitted internal silver plating of the bored inlet hole.

The modifications which permitted silver lining throughout the warm boron trichloride contact areas are shown diagrammatically in Figure 30, with further details in Figure 31.

3. Hydrogenation Catalyst

The only form of hydrogenation catalyst used in this work was 20 mesh, fine silver screen, made of 0.014 inch diameter wire. This screen, obtained in large screen sections, was sized for insertion in the 5/8 inch, 1 inch and 1/2 inch diameter reactors by punching out circular sections with appropriately sized dies. Silver screen from both Newark Wire Cloth Company and Cleveland Wire Cloth Company was used without discrimination.

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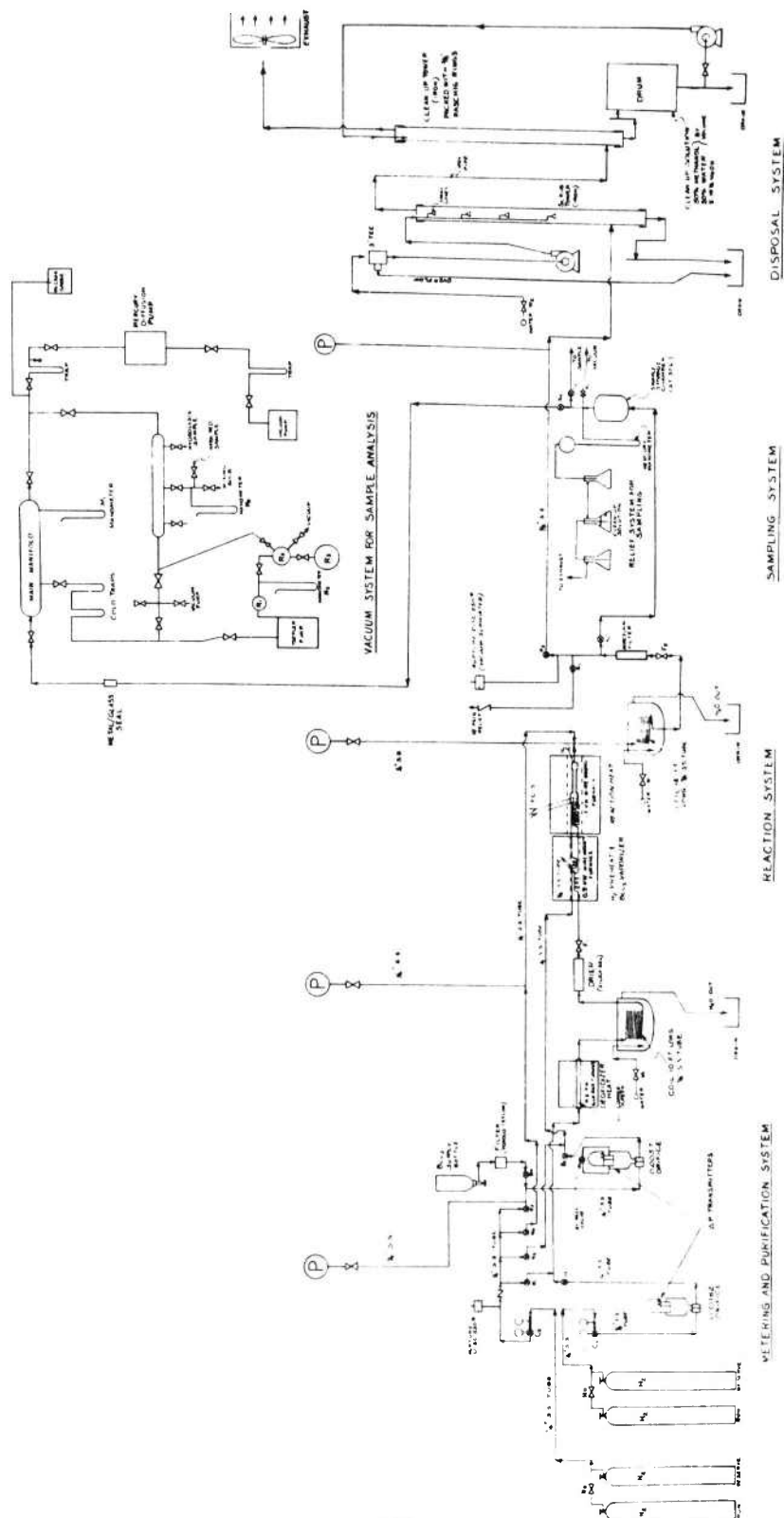


FIGURE 26. SCHEMATIC FLOWSHEET: REACTION EQUIPMENT, HYDROGENATION OF BORON TRICHLORIDE

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TABLE 37
Details of Reactors Used in Hydrogenation of BCl₃

Letter Designation	Figure No.	Materials of Construction		Inside Dimensions			Runs
		Basic Metal	Plating or Lining	Dia. (in.)	Length (in.)	Volume (cu.in.)	
A	27	C-Steel	None	5/8	9	2.8	100 through 207
B	27	Stainless Steel AISI Type 347	None	5/8	9	2.8	208 through 310 402
C	28	Nickel Type "A"	None	5/8	9	2.8	401, 403, 404
D	28	Nickel Type "A"	Silver Plated (0.001 in.)	5/8	9	2.8	(405), 406, 407
D	28	Nickel Type "A"	Re-Silver Plated (0.003 in.)	5/8	9	2.8	408 through 510 601
E	29	Stainless Steel AISI Type 347	Silver Plated	1	7	5.5	511 through 513 602
F	29 31	Stainless Steel AISI Type 347	Silver Lined 5/64" thick	1/2	7	1.4	903 through 1401

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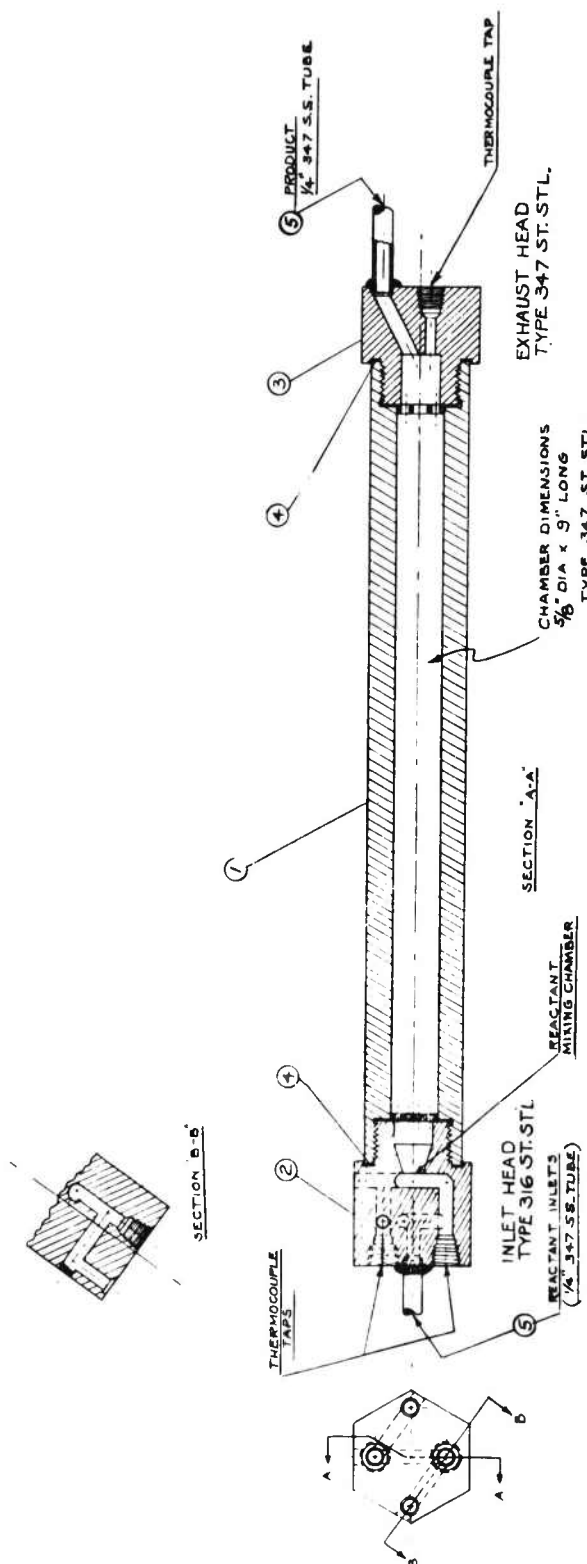
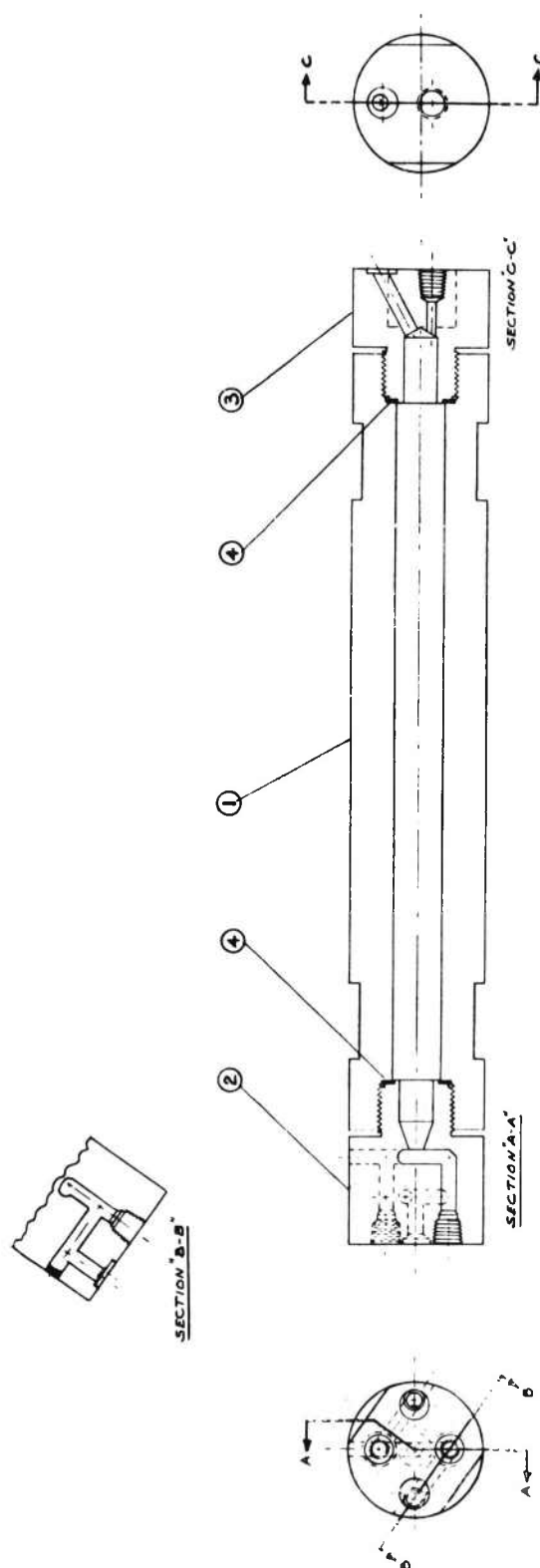


FIGURE 27. REACTION CHAMBER, HYDROGENATION OF BORON TRICHLORIDE

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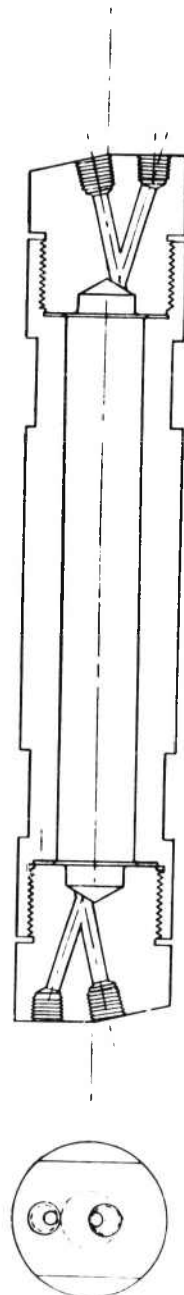
(Note: Chamber Dimensions - 5/8" x 9" long)

FIGURE 28. REACTION CHAMBER

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CHAMBER DIMENSIONS: 1" I.D. x 7" LONG.

FIGURE 29. REACTION CHAMBER - MODIFICATION 2

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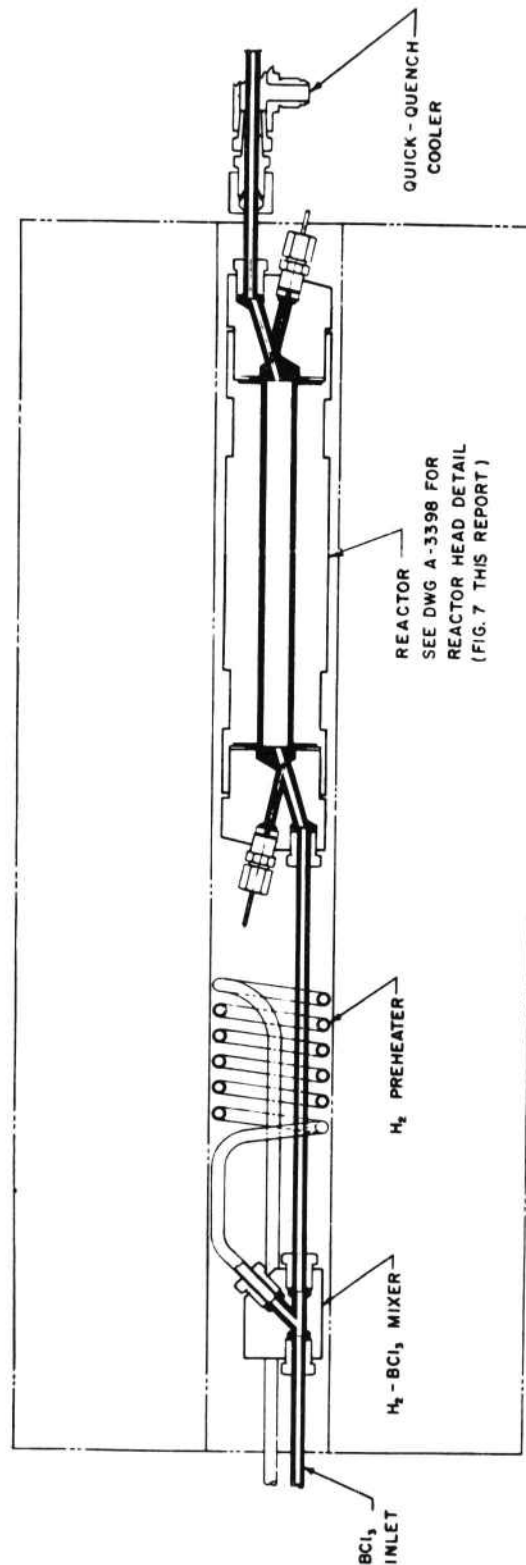
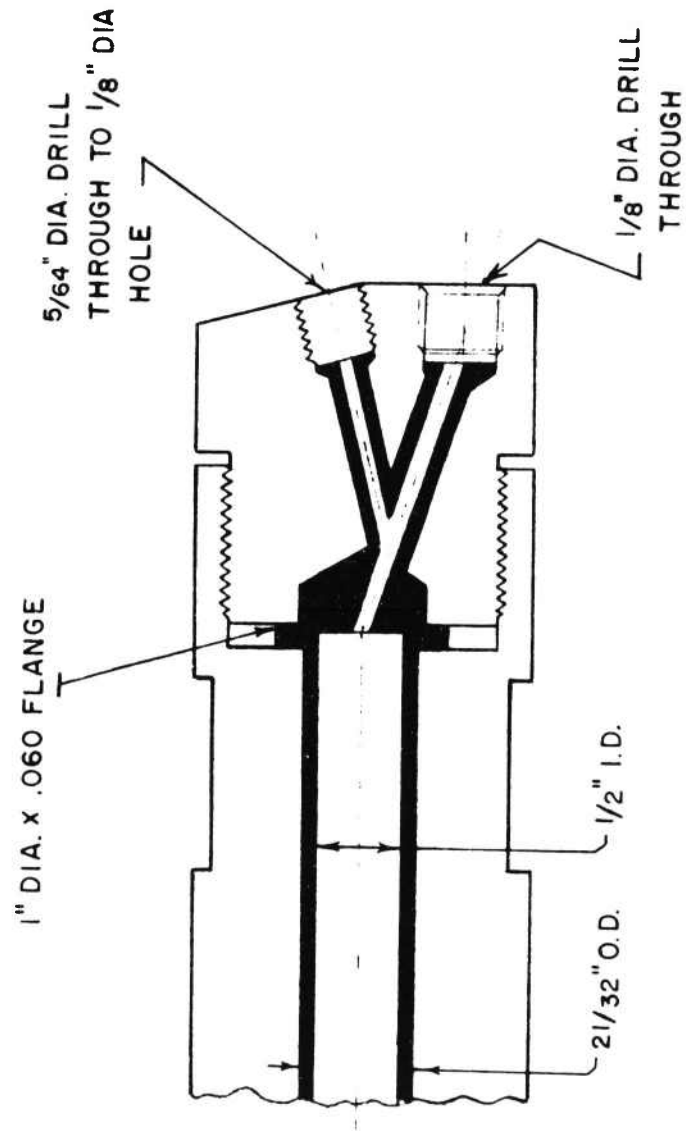


FIGURE 30. DIAGRAM OF H_2 PREHEATER AND SILVER-LINED MIXER AND REACTOR

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99% PURE SILVER LINING

FIGURE 31. REACTOR HEAD, SILVER-LINED ASSEMBLY

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The cut screens were pretreated by rinsing with trichloroethylene, then with Nacconol detergent, and then water. Those which were used in Runs 308 through 612 were immersed in HNO_3 (5 N) for one minute. Following this, they were rinsed in deionized water, then acetone. Finally, they were dried by blowing with N_2 . The immersion in nitric acid was discontinued for the catalyst batch which was charged new with Run 903.

4. Analytical

The equipment for determining the composition of the five process streams consisted of:

- a. Sampling valves and manifolds and collection "surge" tanks.
- b. Glass vacuum line equipment for volumetric measurement of sample quantities and of condensable and non-condensable components, and for transfer to infrared analysis cells or to special hydrolysis flasks.
- c. Infrared spectrometer.
- d. Hydrolysis flasks with connectable gas measuring equipment and with conventional acid-base titration equipment.

Details of the analytical equipment are given in Appendix F.

B. Discussion

As might be expected, a number of runs was necessary before it was possible to carry out experiments on reasonably routine basis. The results from these 17 preliminary runs are presented in Table 38.

The following specific improvements in equipment and in procedures resulted:

1. Improved method for elimination of residual water and air from all parts of the piping system prior to the introduction of BCl_3 .
2. Installed pipeline filters before liquid BCl_3 .
3. Changed design of gas disposal scrubbers.
4. Eliminated 1/8 inch O.D. tube size from use in preheater tube coils.
5. Lower permissible temperature to be reached by BCl_3 before it was mixed with H_2 .

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TABLE 38
PRELIMINARY RUNS: HYDROGENATION OF BCl_3 IN VOID REACTOR

RUN NO.	H_2 RATE ^(a)	NOMINAL MOLE RATIO ($\text{H}_2:\text{BCl}_3$)	REACTOR TEMPERATURE ^(b)			REMARKS
			H_2 INLET	BCl_3 INLET	REACTOR OUTLET	
100						Plug-up 1/8" O.D. BCl_3 preheater tube. Furnace may have been 2000°F.
101	0.12	11	800	-	1200	No BCl_3 vaporizer. Flows were irregular.
102	0.12	16	750	150	1000	BCl_3 vaporizer installed.
103	0.12	16	750	200	1100	Poor temperature control.
104	0.12	11	900	-	1200	Plug-up packed water scrubber in disposal train.
105	0.12	-	-	-	400	Plug-up packed water scrubber in disposal train.
106	0.12	10	-	-	1150	Water scrubber bypassed for this and runs 107-201. Filter in service before flow-regulating valve, H_2 . Smoother flow control.
107	0.12	-	-	-	1000	Plug-up 1/8" O.D. H_2 preheater tube.
Operating Improvements: Add H_2 deoxidation and drying, improve temperature control, disassemble and clean all equipment.						
108	0.12	11	750	880	1100	First product samples for infra-red spectra analysis.
201	0.12	11	900	1000	1100	Product samples. Premature shutdown. NaOH scrubber blew over.
202	0.12	11	1100	1250	-	Product samples. Reinstall water scrubber, this time with sprays, for this and all succeeding runs.
203	0.12	10	930	1020	1100	Type 304 stainless steel BCl_3 inlet tube broke open. Both BCl_3 and H_2 inlet tubes were brittle. Outlet tube was O.K.
204	-	-	-	890	1300	Plug-up 1/8" O.D. BCl_3 preheater tube. Preheat furnace 1000°F.
205	0.12	11	800	850	1260	Plug-up new 1/8" O.D. BCl_3 preheater tube.
206	-	-	925	-	1370	Plug-up 1/8" O.D. H_2 preheater tube.
207	0.12	11	800	-	1300	Plug-up 1/8" O.D. BCl_3 preheater tube, even after special start-up precautions.
Revamp Preheater Arrangements: Use 1/4" O.D. Type 347 stainless steel instead of 1/8" O.D. for BCl_3 and H_2 preheater coils, place preheater furnace adjacent to reactor furnace to eliminate air-cooling of tubing between furnaces.						
Use New Type 347 Stainless Steel Reactor						
208	0.12	10	1350	1380	1300	Burn out new 1/4" O.D. BCl_3 tube near reactor after 20 minutes of BCl_3 flow.

Before next run, reduce travel of BCl_3 tube within reactor furnace. Plan lower reaction temperatures.

(a) lb. moles/hour

(b) Thermocouple readings, °F. (approximately)

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Changes (1), (2) and (3) virtually eliminated shutdowns due to B_2O_3 or H_3BO_3 plugging, whereas changes (4) and (5) eliminated shutdowns due to $FeCl_2$ formation.

Installation of deoxidation and drying equipment for the H_2 feed was also a desirable improvement. However, the particular contribution to attainment of satisfactory operating conditions cannot be isolated.

After the preliminary runs, seven hydrogenation runs were made using a reactor which contained no silver catalyst, and 51 hydrogenation runs were made using a silver catalyzed reactor. Pertinent data for these runs are tabulated in Tables 39, 40 and 41.

1. Conversion to $BHCl_2$

a. Effect of Feed H_2/BCl_3 Ratio

The effect of increasing the feed H_2/BCl_3 ratio is to increase the percentage conversion of BCl_3 to $BHCl_2$ as is shown in Figure 32 for the temperature range $1300^\circ F.$ to $1320^\circ F.$ ($705-716^\circ C$). The nature of this effect is predictable from equilibrium considerations, according to the expression for the equilibrium constant:

$$K_p = \frac{(P_{BHCl_2})(P_{HCl})}{(P_{BCl_3})(P_{H_2})}$$

At R moles H_2 per 1 mole BCl_3 in the feed, and at conversion to X moles $BHCl_2$ per initial mole BCl_3 , this expression becomes:

$$K_p = \frac{(X)(X)}{(1-X)(R-X)}$$

which is independent of total pressure. The values for this expression

$$\frac{(X)(X)}{(1-X)(R-X)}$$

calculated from the curve drawn through the data on Figure 32 fall within 10 per cent of the number 0.017. This apparent correlation suggests that the reactor products whose compositions fell near the curve were near equilibrium at the reactor outlet temperature.

b. Effect of Temperature

The effect of increasing the temperature of reactor products is to increase the percentage conversion of BCl_3 to $BHCl_2$ as shown in Figure 33 for feed $H_2:BCl_3$ ratios of approximately 15:1. This qualitative effect had also been observed in laboratory experiments.

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The conversions obtained at 1420°F. are less than predicted by the curve. Whether this represents a failure to reach equilibrium, possibly due to a change in catalyst structure or whether equilibrium at 1420°F. occurs at lower conversions than the curve shows, can only be answered by a thermodynamic calculation beyond the scope of this work. The question is largely academic anyway since design and materials considerations limit the temperature of a practical reactor to about 1300°F.

The general effect of reducing the inlet temperature below the reactor discharge temperature was to reduce the conversion to BHCl_2 as shown by Figure 33.

For purposes of characterizing the reaction temperature of a run in which the $\text{H}_2:\text{BCl}_3$ ratio was 15:1 or higher, the average value of the inlet H_2 temperature and the reactor discharge temperature was used.

3. Effect of Catalyst vs. No Catalyst

The advantage of using silver catalyst in the hydrogenation reactor could not be conclusively demonstrated by the data obtained in the prepilot plant because there were too few void reactor runs, and temperatures were not identical with those which were maintained for otherwise comparable catalytic runs.

The five most consistent results of the silver catalyzed runs, plotted in Figure 34, have an average of about 20 per cent conversion at an average temperature of about 1120°F. (604°C). For comparison, the five most consistent results of the non-catalyzed runs have an average of about 10 per cent conversion at an average temperature of about 1050°F. (566°C).

This difference in per cent conversion does not show a decisive advantage for the use of catalyst at 1050°F. to 1120°F., inasmuch as it is about the same that would be expected (Figure 33) in comparison of catalyzed conversions at 1120°F. and 1050°F.

The residence times for the void and for the catalyzed runs are within the same general limits, 0.19 to 0.43 second.

4. Effect of Catalyst Pretreatment

Of the nine runs which were made with fresh batches of catalyst, only two resulted in conversions to BHCl_2 which were as good as the conversions obtained in runs made with twice-used catalyst.

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TABLE 39

Conversion Results: Runs with Void Reactor
(Reactor Designation "B"; see Table 37 for details)

Run No.	Press. (psig)	Product Gas Composition (by Infrared)							Metered H ₂ Rate				Calc. BCl ₃ Rate				Residence Time (a) (seconds)
		Temperature (°F.)			BCl ₃ (Mole %)	BHC1 ₂ (Mole %)	Calc. Feed Ratio (H ₂ /BCl ₃)	H ₂ Rate (lb. moles per hour)	BCl ₃ Rate (lb. moles per hour)	BCl ₃ Rate (lb. moles per hour)	BCl ₃ Rate (lb. moles per hour)	BCl ₃ Rate (lb. moles per hour)					
		H ₂ Inlet	BCl ₃ Inlet	Reactor Outlet													
301	100	1010	920	1100	7.1	0.73	12	0.105	0.0089	0.0089	0.0089	0.0089	0.36				
302	100	995	940	1030	8.2	0.48	11	0.102	0.0098	0.0098	0.0073	0.0073	0.38				
303	100	1040	1010	1000	7.8	1.10	10	0.103	0.0101	0.0101	0.0097	0.0097	0.37				
304	50	1060	1060	1000	5.0	0.46	17	0.090	0.0053	0.0053	0.0096	0.0096	0.24				
305	50	1060	950	1010	11.5	1.05	7	0.090	0.0130	0.0130	0.0096	0.0096	0.24				
306	50	1060	940	1050	10.2	1.55	8	0.090	0.0120	0.0120	0.0096	0.0096	0.23				
307	100	1120	1110	1100	6.4	0.88	13	0.102	0.0080	0.0080	0.0073	0.0073	0.36				

(a) Sample Calculation of Residence Time

For Run 301:

$$\text{Volume rate of reactor gas} = \frac{0.105 + 0.002}{3600} \times 359 \frac{\text{CF}}{\text{lb. mole}} \text{ (at std. cond.)} \times 1728$$

$$\times \frac{14.7}{114.7} \times \frac{460 + 1055}{492} = 7.75 \frac{\text{cubic in.}}{\text{sec.}}$$

$$\text{Residence Time} = \frac{2.8 \text{ cu. in. (Reactor Volume)}}{7.75} = 0.36 \text{ seconds}$$

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TABLE 40
CONVERSION RESULTS: RUNS USING SILVER SCREEN CATALYST
(H₂:BCl₃ RATIOS OVER 13:1)
(REACTOR PRESSURE IN ALL RUNS 100 psig)

RUN NO.	REACTOR ^(a)	TEMPERATURE (°F)		PRODUCT GAS COMPOSITION				METERED H ₂ RATE (lb. mole/hr)	CALCULATED BCl ₃ RATE (lb. mole/hr)	METERED BCl ₃ RATE (lb. mole/hr)	RESIDENCE TIME (sec)
		H ₂ INLET	BCl ₃ INLET	REACTOR PROD.	BCl ₃ (mole %)	BHCl ₂ (Mole %)	% CONVERSION	CALC. FEED RATIO (H ₂ :BCl ₃)			
308	B	1120	1090	1090	5.8	1.61	22	13	0.0080	0.0073	0.27
310	B	1130	1090	1090	4.8	1.10	19	16	0.0063	0.0073	0.27
401	C	1080		1150	5.4	0.43	7	16	0.0064	0.0073	0.27
402	B	350		1100	5.9	0.00	0	16	0.0064	0.0073	0.36
403	C	880		1180	6.5	0.55	8	13	0.0078	0.0073	0.29
406	D	670		1080	7.0	0.15	2	13	0.0079	0.0073	0.32
407	D	1100		1280	5.0	1.74	26	14	0.0074	0.0073	0.26
408	D	990		1200	5.5	0.78	12	15	0.0069	0.0073	0.28
409	D	930		1230	5.2	1.54	23	14	0.0101	0.0099	0.26
410	D	1030		1210	2.5	1.30	34	25	0.0025	0.0046	0.45
411	D	1110		1120	4.7	0.95	17	17	0.0062	0.0073	0.27
412	D	1180		1120	5.8	1.31	18	13	0.0107	0.0089	0.19
413	D	1120		1120	5.4	1.30	19	14	0.0045	0.0051	0.43
501	D	1330		1320	2.7	1.90	41	21	0.0049	0.0073	0.25
502	D	1330		1320	2.5	2.15	46	20	0.0069	0.0089	0.18
503	D	1310		1320	3.9	2.21	36	16	0.0041	0.0051	0.39
504	D	1350		1320	3.6	2.54	41	15	0.0067	0.0073	0.24
505	D	1340		1320	3.7	2.68	42	15	0.0094	0.0089	0.17
506	D	1330		1320	3.9	2.58	40	14	0.0044	0.0051	0.38
507	D	1310		1320	3.9	2.69	41	14	0.0072	0.0073	0.24
508	D	1300		1320	4.7	2.28	33	13	0.0105	0.0089	0.18
509	D	1310		1320	4.1	1.88	31	16	0.0040	0.0051	0.39
510	D	1330		1320	2.1	2.36	53 ^(d)	22	0.0047	0.0073	0.25
511	E	1360		1420	4.3	2.27	35	14	0.0072	0.0073	0.45
512	E	1330		1420	3.4	2.44	42	16	0.0086	0.0089	0.34
513	E	1320		1420	3.6	2.44	40	16	0.0041	0.0051	0.74

(a) See Table 37 for details.

(b) Infra red analysis.

(c) See Table 39 for footnotes which give sample calculation of Residence Time.

(d) Note that the catalyst (40 screens per inch, 0.014" diameter wire 20 mesh) occupies 25% of volume. Run 510 differed from all other runs shown in this table in that the catalyst occupied only five inches of reactor volume and also contained a small amount of silver screen. The catalyst was a silver screen. The catalyst was a silver screen. The catalyst was a silver screen.

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TABLE 41

CONVERSION RESULTS: RUNS USING SILVER CATALYST

(Reactor Designation: "F" - See Table 37)
 (Reactor Pressure: 85 psig)
 (Reactor Temperature: 1300°F - Both Inlet and Outlet)
 (H₂:BCl₃ Ratios Between 0.6 and 4.4)

RUN NO.	METERED H ₂ RATE (lb. mole/hr.)	PRODUCT GAS COMPOSITION ^(a)			CALC. BCl ₃ RATE (lb. mole/hr.)	METERED BCl ₃ (lb. mole/hr.)	RESIDENCE TIME ^(b) (sec)
		BCl ₃ (mole-%)	BHCl ₂ (mole-%)	CALC. FEED Ratio H ₂ :BCl ₃			
903	0.065	23.3	2.8	2.8	0.023	0.0220	0.13
904	0.065	22.7	4.05	2.7	0.024	0.0220	0.13
905	0.065	20.9	4.6	2.9	0.022	0.0220	0.13
906	(0.01) ^(c)	55.2	6.3	0.63	-	0.0163	(0.43)
907	0.061	16.9	4.9	3.6	0.017	0.0163	0.15
908	0.050	23.8	5.25	2.4	0.021	0.0196	0.16
1001	0.022	17.7	4.7	3.4	0.0065	0.0062	0.40
1002	0.022	16.7	4.7	3.7	0.0060	0.0062	0.41
1003	0.022	15.6	4.7	3.9	0.0056	0.0062	0.41
1004	0.022	14.1	4.4	4.4	0.0050	0.0062	0.42
1005	0.022	14.4	4.48	4.3	0.0051	0.0081	0.42
1101	0.022	32.5	5.33	1.6	0.014	0.0081	0.32
1102	0.022	20.5	5.26	2.9	0.0076	0.0074	0.38
1103	0.022	19.9	5.20	3.0	0.0073	0.0074	0.39
1104	0.022	21.0	5.06	2.8	0.0079	0.0074	0.38
1201	(0.023) ^(d)	19.9	5.10	3.0	-	0.0074	(0.37)
1202	0.022	16.1	4.45	3.9	0.0056	0.0074	0.41
1203	0.023	32.4	4.83	1.7	0.0135	0.0074	0.31
1204	(0.016) ^(e)	48.9	4.26	0.9	0.018	-	(0.33)
1301	0.030	17.3	5.03	3.5	0.0086	0.0083	0.29
1302	0.062	17.4	5.1	3.4	0.018	0.0171	0.14
1303	0.062	18.2	4.24	3.5	0.018	0.0171	0.14
1304	0.062	20.1	4.98	3.0	0.021	0.0171	0.14
1305	0.062	18.2	4.91	3.3	0.019	0.0171	0.14
1401	0.062	17.7	5.11	3.4	0.018	0.0171	0.14

(a) Infra-red analysis

(b) See Table 39 footnote for Residence Time calculation method.

(c) Defective H₂ flowmeter. H₂ rate calculated from metered BCl₃ rate and analyzed H₂:BCl₃ ratio.(d) H₂ rate measurements were not internally consistent. Calculated as in (c).(e) H₂ rate measurements were not internally consistent. Calculated by subtracting H₂ which was metered to absorber from H₂ which was removed from supply cylinder.

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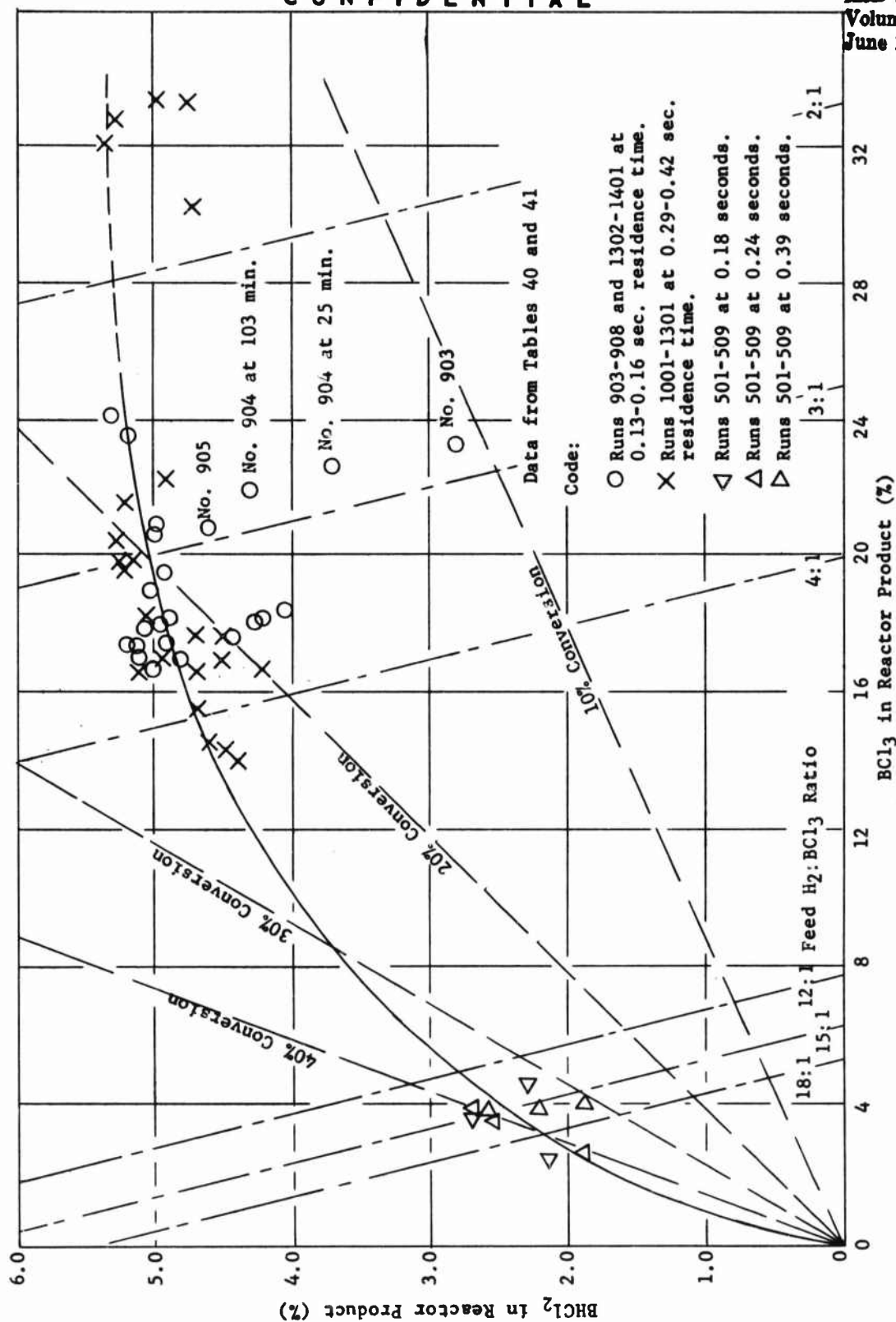


Figure 32. Conversion to BCl₂ vs. Ratio H₂:BCl₃ in Feed at 1300-1320°F., 85-100 psig.

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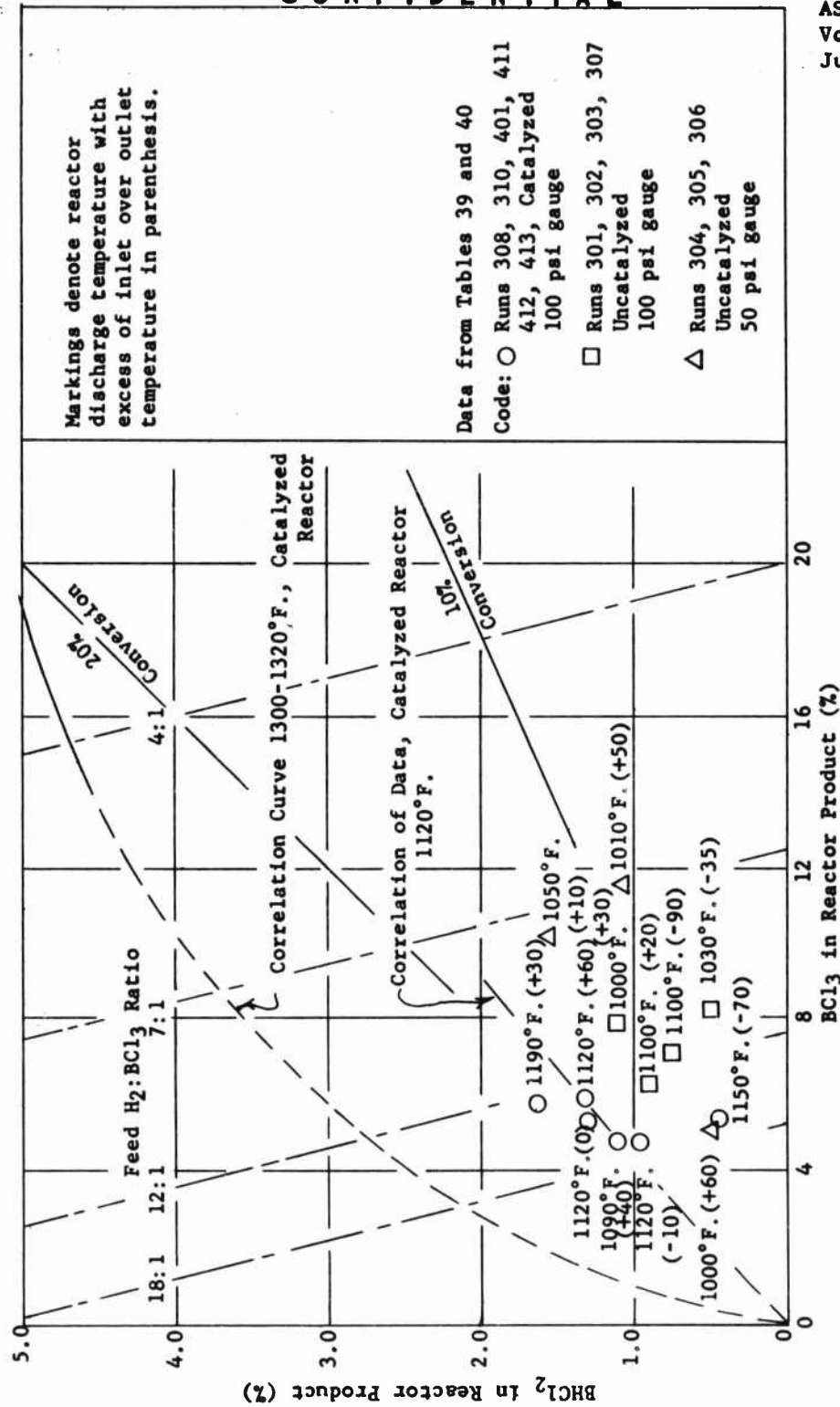


Figure 34. Comparison of Conversions to BCl₂ for Catalyzed and Uncatalyzed Reaction

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The fact that conversions improved until the second or third reuse of the catalyst in Runs 408 through 509, Runs 511 to 513, and Runs 903 through 1401 indicates that silver has a definite catalytic effect; otherwise there would be no change. The fact that induction runs were required for development of maximum catalytic activity in these three batches, but apparently not for the batches used in Runs 308 and 310, indicates that the initial catalyst surface was different in Runs 408, 511 and 903 from that in Runs 308 and 310. However, the only known change in pretreatment was the omission of the nitric acid pretreatment step before Run 903, but the conversion behavior following this run was not distinctive from the conversion behavior following Runs 408 and 511.

5. Catalyst Life

The fresh silver catalyst which was charged into the hydrogenation reactor for Run 903 was used without change through Run 1204, for a net cumulative service of 73.6 hours. At this time the first 1-1/4 inches of the 7-1/4 inch bed was replaced so as to serve as a fresh filter to test for corrosion products from upstream. Later, after Run 1305, at a net cumulative service of 103.9 hours for the main part of the bed, the first 1/2 inch was again replaced to serve as a fresh filter. At the conclusion of the last run, Run 1401, the major 6 inch portion of the catalyst bed had a net cumulative service of 109.1 hours and showed no change from its initial appearance. This fact indicates a catalyst life at the temperature of these runs (1300°F. or 704°C) far in excess of this net 4-1/2 day period.

The black coating which was found on the initial screens at 73.6 cumulative hours and at 103.9 hours was easily traceable to corrosion of exposed stainless steel surfaces and was not due to any direct attack of the silver catalyst by the reacting gas mixture.

6. Loss in Yield of Boron Chlorides

No direct measurement was made of the total rate of flow of reactor products. Hence no direct calculation of the loss in yield of boron chlorides was possible.

However, many indirect calculations were made in studying the reliability of the calculated material balances. In these calculations no systematic deviation was detected which could be ascribed to loss in yield of boron chlorides. Inasmuch as no accretion of by-products was found in the reactor or in the equipment or the filter after the reactor after the 109 hours, it must be assumed that any loss in yield of boron chlorides in the hydrogenation step is very low. During this 109 hour cumulative period, the total weight of boron trichloride charged to the reactor was approximately 170 pounds.

C O N F I D E N T I A L

7. Effects of Operating Pressure

The only data on the effect of operating pressure are those shown in Figure 34 for Runs 304 to 306. Reducing the pressure from 100 psi gauge to 50 psi gauge in a void hydrogenation reactor had no discernable effect on the BHCl_2 conversion.

8. Effect of Residence Time

The maximum variation in residence time among these hydrogenation runs, namely from 0.13 to 0.74 second, was not enough to produce a measurable effect upon the conversion to BHCl_2 .

This is shown in Figure 32 for runs at 1300°F. to 1320°F. (704-716°C). The three ratios, 0.18, 0.24 and 0.39 second, for the nine runs at H_2/BCl_3 ratio near 15:1 are shown by differently oriented triangles. The two principal rates, 0.13 to 0.16 second and 0.29 to 0.42 second, for the runs at H_2/BCl_3 ratio near 3:1 are shown by crosses and circles. The correlation curve which is drawn represents one group of points as well as it represents the other group.

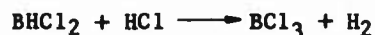
9. Pressure Drop in Silver Catalyst Bed

The pressure drop of the reaction gases passing through the silver screen catalyst bed was measured with a special differential pressure gauge starting with Run 1001. No pressure drop was detectable in Runs 1001-1005 which were typical of operation at total gas throughput of 0.028 lb. moles per hour.

The value of 2 psi obtained in Runs 1304-1401 is the upper limit which may be ascribed to pressure drop in the catalyst screen when the total gas throughput was 0.075 lb. moles per hour, inasmuch as it may also have been due to other minor obstructions in the flow system.

10. Quenching of Reactor Products

The residence time of the reactor product gases in the water cooled quenching tube was always too short to provide a test of the reaction rate information obtained previously in the laboratory for the back reaction:



The maximum residence time of the reactor product gas within this tube was calculated to have been approximately 0.3 second during Runs 1004 and 1005. Even if this gas had been at an average effective temperature of 400°C during this time, the reaction rate constant, k , in the equation:

$$\frac{dP_{\text{BHCl}_2}}{P_{\text{BHCl}_2}} = k P_{\text{HCl}} d\theta$$

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would have been only 7×10^{-3} (mm.-min.)⁻¹; according to the laboratory data. For this constant, the fractional loss in BHCl_2 content was calculated to be 0.008 (or 0.8%) at 4.48 mole fraction HCl , 100 psi absolute total pressure, and 0.3 second. This represents too small a loss to be detected.

The two catalyzed conversion runs, Runs 308 and 310, at 1090°F. were made before the water cooled quencher was installed and were therefore cooled a little more slowly. However, the results do not show a possible loss of conversion due to slow cooling, by reference to either Figure 33 or Figure 34.

C. Chemical Attack on Equipment

Several metals were evaluated for reactor construction and chemical attack of the hydrogenation equipment was observed in many forms. The results of this testing program, as reported in the following paragraphs, led to the selection of silver lined equipment for all service in contact with heated BCl_3 vapor. Further, the uncertain behavior of silver during Runs 601 and 602 when in contact with only N_2 at 800°F. (427°C) and 500°F. (260°C) led to the plan to introduce H_2 into the pilot plant BCl_3 vapor stream at a low temperature. Thermodynamic calculations have shown that AgCl cannot exist in equilibrium contact with a reaction mixture containing H_2 when the total pressure is as low as 12 to 13 atmospheres.

1. Corrosion of Carbon Steel Reactor

Preliminary Runs 100 through 207, described in Table 38, were made in the carbon steel reactor. Each time the reactor was inspected, a brownish scale containing much ferrous chloride was found.

2. Plugging and Burnout of BCl_3 Preheater Tube (SS)

During many of these runs the stainless steel 1/8 inch O.D. tube which served as BCl_3 preheater became plugged up. Qualitative analysis of the material which constituted the plug in Run 100 showed that it contained large amounts of ferrous chloride and some form of boron.

Run 208, the last of the preliminary series, was made in the type 347 stainless steel reactor. This run was terminated by the burnout of a portion of the new 1/4 inch O.D. type 347 stainless steel tube through which preheated BCl_3 had flowed for about 20 minutes. The temperature of this point was about 1450°F. Two grams of a black, sooty deposit were recovered from the reactor after this run; however, the reactor walls were relatively unattacked. At the time of chemical analysis the black deposit had the following composition:

C O N F I D E N T I A L

Boric acid oxide	17.0%
HCl	9.0%
Iron chloride (chiefly ferrous)	25.0%
Water insoluble boron	0.7%
Water insoluble iron (magnetic)	31.0%
Other water insoluble material (Cn, Ni, Pb (?), etc.)	17.0%
	99.7%

3. Corrosion Products from SS Preheater Tube

Although no further plugging nor burning-out occurred in the stainless steel, 1/4 inch BCl_3 preheater tube, products of chemical attack of stainless steel were observed both during non-catalyzed Runs 301 through 307 and during the catalyzed runs which followed.

For Runs 301 through 310, the greater portion of the preheater tube was maintained at the BCl_3 preheat furnace temperature of 600°F. (316°C). The remaining portion of this tube which led through 10 inches of the main furnace to the reactor head was hotter because the temperature of the main furnace was approximately 1100°F. (593°C).

Products of chemical attack were observed in the piping system after each of these non-catalyzed runs, Runs 301 through 307. Each time a coating of brownish-red material was found in the lower temperature portions. The amount of this material was sufficient to cause plugging of the stainless steel cooling coil in Run 302. Subsequent chemical analysis of material removed from this cooling coil was:

Boric acid oxide	45.0%
HCl	11.0%
Iron chloride (half ferrous- half ferric)	41.0%
Water insoluble boron	2.2%
Other water insoluble material	<u>1.0%</u>
	100.2%

When silver screen catalyst was used in the stainless steel reactor during Runs 308, 309 and 310, these corrosion products showed up as a black deposit on the first catalyst screens and on the reactor walls in the space before the screens. This deposit could easily be scraped from the screens and was magnetic.

No brownish-red material was found in the lower temperature portions of the piping systems after any catalytic hydrogenation run.

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4. Use of BCl_3 from Different Sources

Information regarding the various sources of BCl_3 used is contained in Table 42. Changing to a more nearly pure grade of BCl_3 , as was done for Runs 309 and 310, did not change the nature nor the amount of the deposits on the initial catalyst screens. Whereas BCl_3 from the Matheson Company had been used for runs through Run 308, BCl_3 from American Potash & Chemical Corporation was used for Runs 309 and 310.

However, direct attack of the silver screens was observed when the BCl_3 was drawn from a new cylinder of Matheson Company BCl_3 and when other equipment and process changes were introduced for Runs 401 through 404. This attack formed a non-magnetic crust on the initial screens and the unattacked silver wire core was smaller than the original silver wire had been.

5. Premixing of H_2 with BCl_3

Premixing the BCl_3 with H_2 in Run 402 so that H_2 was present during all parts of the preheat process did not eliminate the corrosion in the stainless steel system. Deposition of corrosion products was again found on the first silver screens, as noted in Table 43.

6. Corrosion of Stainless Steel Reactor

The stainless steel type 347 reaction chamber which had served during Runs 208 through 310 was not used after Run 402. Although the obvious corrosion products had been traceable in each instance to the preheat piping and possibly to the reactor head, close examination of the chamber wall showed that its surface had also undergone some chemical action.

7. Corrosion of Nickel Reactor

Changing to type A nickel brought increased corrosion which had a different appearance. This occurred in both Runs 401 and 403. In Run 401 nickel was substituted for stainless steel as the reactor and as the lead-in pipe for BCl_3 vapor. The BCl_3 was vaporized as in Runs 301 through 310 in the stainless steel preheater at 600°F . (316°C). In Run 403, H_2 was premixed with BCl_3 , and the mixed gases were led through all nickel piping to the nickel reactor.

8. Behavior of Silver Plated Hydrogenation Equipment

The behavior of silver plated hydrogenation equipment is summarized for Runs 405 through 513 in Table 43. Changing to silver plated equipment in Run 405 gave the first corrosion-free operation of the hydrogenation equipment. Although in subsequent hydrogenation runs corrosion products were found on the initial screens, these could in each instance be traced

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to flaws in the silver covering or, as in Run 407, to a flaw in the covering of the heated stainless steel tubing in contact with BCl_3 at the mixing tee.

Use of 0.003 inch plating rather than 0.001 inch plating on nickel permitted more runs to be made in the equipment before equivalent attack occurred. However, this was only partly successful in eliminating the flaws which developed during operation and maintenance.

Changing to stainless steel as a base for the silver plating permitted high temperature runs to be made with safety. This was done in Runs 511 to 513 and 602. However, in these runs the adherence of the plating to stainless steel proved to be poorer than had been observed for nickel.

9. Behavior of Silver Lined Hydrogenation Equipment

Use of silver as a liner for the reaction system as sketched in Figure 30 gave essentially trouble-free operation during the concluding 25 runs of the prepilot plant program. These runs provided a cumulative service of 109 hours. Inspections of the silver screens at 74 and at 104 hours revealed black coatings, extending one inch and one-half inch, respectively. These may be readily ascribed to flaws which developed in the liners due either to local overheating or to flaws which developed during disassemblies. These disassemblies were necessary for the repair of leaks which developed in thermocouple attachments, threaded joints, and tubing connections.

10. Corrosion of Stainless Steel, Nickel and Monel Samples During Conversion Run

The chemical attack of stainless steel, nickel and monel by the conversion gas mixture and the simultaneous resistance of silver to such attack is shown by the results of Run 510. These are given in Table 44. Attack of the stainless steel screens generated volatile corrosion products, some of which were deposited on the succeeding section of silver screens. On the other hand, both the nickel and the monel screen sections accumulated non-volatile corrosion products.

11. Action of BCl_3 on Silver in the Absence of H_2

The action of BCl_3 on silver in the absence of H_2 was studied in three exploratory runs, Runs 404, 601 and 602. Some of the results are described in Table 45.

Severe attack of the silver occurred in Run 404 when Matheson Company BCl_3 was employed. The BCl_3 was mixed with N_2 at room temperature and the N_2 - BCl_3 mixture was passed into the nickel reactor at 540°F . to 1130°F . (282 - 610°C).

TABLE 42

SUMMARY OF ANALYTICAL DATA ON BORON TRICHLORIDE

SUPPLIER	CYLINDER DESIGNATION	RUNS	ANALYTICAL METHODS	ANALYTICAL RESULTS (mole %)				
				BCl ₃	COCl ₂	SUBSTANCE OF MASS TO CHARGE RATIO 132 + 134 ^(a)	A	HCl ^(b)
Matheson Company	AT-6301	before 304	Mass Spectrometer	98.6	1.2	0.2	-	19
"	AV-2475	not used	"	99.3	0.48	-	-	12
"	AV-2476	304 - 308	"	99.4	0.6	trace	-	11
"	AV-6469	401 - 404	"	99.4	0.52	-	-	5
American Potash	H-58L-1115-119E	2-lb container similar to those used in 309-310 and 406-503	"	78 ^(c)	0.27 ^(c)	-	16 ^(c)	6 ^(c)
				99.8	0.2	-	trace	-
"	5976	"	by APCC	99.3	0.07	-	-	-
"	906	100-lb container similar to those used in 504 and following	by APCC	99.97	0.033	-	-	-

(a) Per analytical report: "An impurity with mass to charge ratio (m/e) of 132 and 134 With indications of 3 chlorine atoms to the molecule. A good guess would be trichloroethane."

(b) Per analytical report: "Reported on HCl-free basis. This gas was reported separately, and not too much reliability can be placed on the concentrations found as its origin is doubtful. The mass spectrometer and all hardware up to the gas cylinder valve were evacuated for ½ to ¾ hour in the 10⁻⁴ mm Hg range. Several "slugs" of BCl₃ were passed through the apparatus to clean up the water and to condition the mass spectrometer. This treatment is usually sufficient in high purity analysis where water is in the 6 - 10 ppm range."

(c) The analytical results which were marked thus were made on a sample drawn from the vapor portion of the container.

TABLE 43

APPEARANCE OF EQUIPMENT AND CATALYST AFTER CONVERSION RUNS

Runs in Series	Reactor	BCl ₃ Source	Preheating Before Mixing	Reactor Outlet T.C. Rdg. °F	Approx. Con. to BCl ₂ (%)	POST-RUN CONDITION OF EQUIPMENT AND CATALYST			
						Mixing Section	Reactor Walls	CATALYST FIRST SCREENS REMAINDER OF SCREENS	
300- 307	"B"(S.S. Type 347)	Math. #6301 (through 307) Math. #2476	BCl ₃ to 600°F in S.S. H ₂ to 1000°F for 1100°F	1000°F to 1100°F	6 to 13	Slight dark deposits in reactor. Red deposits in the cooler down- stream portions of equipment.	No catalyst used.		
308	Same	Math. #2476	Same	1100°F	13	Black powder deposit in inlet of reactor. Very little attack of reactor walls.	Black powder deposit	No deposit in remainder of bed	
309- 310	Same	Trona 1st lb.	Same	1100°F	16	Same	Same	Same	
402	"B" S.S. Type 347	Math. #6469	No preheat, mix cold	1100°F	0 - 4		Dark coat. "Hard", not sooty; screens brittle		
401	"C" Nickel, Type A	Math. #6469	BCl ₃ to 600°F in S.S. H ₂ to 1100°F	1150°F	7 - 18	At 1": yellow deposit. Outlet tube: gray powder	Sooty deposit, screens brittle	Bronzed	
403	"C" Nickel, Type A	Math. #6469	No preheat, mix cold	1180	6 - 8	Inlet: "extraneous" matter, olive color, blue-green crystals. Middle: drab yellow coat, shiny crystals. Discharge: light olive color, silvery crystals.	Dark coat. Screens brittle less than in 402.	Bronzed, less than in 401.	
405- 406	"D" Agplated Nickel(ca. 1 mil)	Trona 1st 2-lb.	No preheat, mix cold	1080	2	Spotless	Spotless, shiny	Spotless shiny	
407	"D" Agplated Nickel(ca. 1 mil)	1st 2-lb.	Preheat H ₂ only. BCl ₃ inlet is S.S.	1280	18 - 25	Dark coat in S.S. pipe at mixing tee	Some of wall is losing silver plate	Slight coat, dark, sootlike	High polish except slight bronze on exhaust screen.
408- 410	"D" Agplated Nickel(ca. 3 mils)	Trona 2nd 2-lb.	Preheat H ₂ only BCl ₃ inlet is Agplated	1200- 1230	12-34		clean	1st 5: slightly discolored	clean
411- 413	"D" Agplated Nickel(ca. 3 mils)	Trona 2nd 2-lb.	Preheat H ₂ only BCl ₃ inlet is Agplated	1120	16-19		clean	1st 8: very slight darkening	clean
501- 509	"D" Agplated Nickel(ca. 3 mils)	Trona 2nd 2-lb. and 1st 100-lb.	Preheat H ₂ only, BCl ₃ inlet is Agplated	1320	31-46	Some Agplate is off flare of tube before mixing tee	1st 1/16": Ag plate had chipped off. 1st 1/2" - had dark gray coat	1st 28: slight darken- ing. Rubbed off by hand	Highly polished
510	"D" Agplated Nickel	1st 2-lb	Preheat H ₂ only BCl ₃ inlet is Agplated	1320	(50-56)	Contained an assortment of materials.		1st 12: sooty black coating	Ag screens had high polish
511- 513	"E" Agplated S.S.	1st 2-lb	Preheat H ₂ only. BCl ₃ inlet is Agplated	1420	36-45	BCl ₃ tube had dark bygro- scopic deposit in line to reactor	Inlet Passage: Some Agplate had come off. 1st 1/2": dark deposit. Distributor: (1st use) had dark, non-mag- netic powder. Exhaust: screen had mag- netic scale opposite head of reactor which had no plate	1st 20: slight deposit, black, non- magnetic powder	Very slight yellow cast

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TABLE 44

Results of Run 510

Exposure of various materials to H_2-BCl_3 reaction (1.9 hrs. at 1325°F., 15:1 mole ratio $H_2:BCl_3$).

Note that each odd inch of length in the 5/8 inch diameter silver plated nickel reactor was filled by 40 silver screens. Each of the intervening inches was filled as listed below.

Number of Inch	Material	Weight Before Run (gms.)	Change in Weight (gms.)	Description of Appearance Following Run
1st	40 silver screens	12.2	+ 0.02	First 12 screens: sooty black coating. Remainder: highly polished.
2nd	4 pieces, Type 347 SS tube	12.2	+ 0.09	On tubes: loose gray magnetic scale.
3rd	40 silver screens	12.2	-0.08	First screens: gray magnetic deposits. Remainder: shiny.
4th	36 Type 316 SS screens	12.1	-0.56	First screens: slight trace of silver. On all: gray cast, magnetic when rubbed off.
5th	40 silver screens	12.2	+ 0.08	First screens: gray powder coat, not easy to rub off. Remainder: shiny.
6th	36 nickel screens	13.9	+ 1.22	All screens: extremely brittle. Not strong enough to be removed whole.
7th	40 silver screens	12.2	-0.01	All shiny.
8th	30 monel screens	13.9	+ 0.49	First three: gray-white coat. (a) All: slightly darker, somewhat brittle, removable intact.
9th	40 silver screens	12.2	+ 0.01	All shiny.
		113.1	+ 1.26	

(a) The gray-white coat on the monel screens was insoluble both in 10% HNO_3 and NH_4OH . Hence presumably it is neither Ag nor $AgCl$.

TABLE 45
Appearance of Equipment after BCl_3 Exposure in Absence of Hydrogen
(N_2 carrier gas - silver screen catalyst in reactor)

Run No.	Reactor	BCl_3 Source	Preheating Before Mixing	Maximum Reactor T.C. Temp. ($^{\circ}\text{F.}$)	Post-Run Condition of Equipment and Catalyst		
					Reactor Walls	First Screens	Remainder of Screens
404	Nickel Type A	Mathe. No. 6469	No preheat mix cold	1130 (Inlet temp. 540°F.)	Inlet head: heavy black deposit contains metallic silver. 1st 1": approx. 1/32" thick coating. H_2S odor when coating was scraped. Exhaust Head: olive and silver gray with sparkling crystals.	Coated and corroded away	Below 1-3/4" slight uniform color
601	Ag-plated Nickel	Trona, first 100-lb.	Preheat N_2 only. BCl_3 inlet is Ag-plated	800	1st 1/2": uneven bumpy deposit, "non-descript" color	1st 25: gray-brown coating which would not rub off.	
602	Ag-plated Type 347 SS	Trona first 100-lb.	Preheat N_2 only. BCl_3 inlet is Ag-plated	500	Reactor Head: 50% of Ag plate had been removed.	Slight darkening	All screens were dulled

No other experiments were made in which Matheson Company BCl_3 was in contact with silver in the absence of H_2 .

Little, if any, attack was observed in Runs 601 and 602 when American Potash & Chemical Corporation BCl_3 was employed. The BCl_3 was mixed with preheated N_2 and the N_2 - BCl_3 mixture was passed into the silver lined reaction equipment at 800°F. (427°C) and at 500°F. (260°C), respectively.

In addition to these observations, examination of the BCl_3 inlet to the silver lined mixing tee from Runs 903 through 1401 showed that it had undergone little if any attack. The silver lined tubing at this point reached some indefinite temperature which was much higher than room temperature, and it contained BCl_3 now mixed with H_2 .

Uncertainty still remains concerning the permissible limits of impurities in the commercial BCl_3 . The chemical attack of the initial Ag screens in Runs 401, 402 and 403 which occurred in the presence of H_2 was readily distinguishable from the deposits of stainless steel corrosion which occurred in other runs. Boron trichloride from the particular container of Matheson Company BCl_3 used only for Runs 401 through 404 showed no obvious analytical differences from BCl_3 drawn from the supply containers for previous runs.

Loss in yield of boron chlorides and loss of HCl was anticipated when stainless steel, nickel and monel were used as substitutes for silver plated or silver lined equipment. The only quantitative indication of this occurrence was in Run 510, when stainless steel, nickel and monel were all inserted in place of some silver screens in the hydrogenation reactor. The apparent decrease in total boron content of reactor products and the apparent loss of an appreciable amount of HCl are consistent with the anticipated results. Calculated BCl_3 rate was lower relative to metered BCl_3 rate for Run 510 than for the other runs in the series, Runs 401 through 513. The loss of HCl is deduced from the fact that the per cent conversion to BHCl_2 , 53 per cent, was higher than for any of the all silver runs. Loss of the HCl by reaction with the metal would shift the equilibrium to higher conversion.

II. Integrated Process

A. Equipment

The general arrangement of the prepilot plant equipment is shown as a simple flow diagram in Figure 35.

Hydrogen, purified as before, was passed through a preheater and silver lined reactor, which were arranged as shown in Figure 35. It could then react

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with BCl_3 , with which it was mixed in a tee located at the entrance of the furnace section.

The reactor products, H_2 , BCl_3 , dichloroborane (DCB) and HCl then entered the primary absorber at about the midpoint. A separate stream of liquid BCl_3 absorbent was fed to the top of the primary absorber in order to remove DCB from the gas, leaving as absorber overhead the gases H_2 , BCl_3 and HCl .

The liquid mixture of BCl_3 and DCB which dripped to the lower section of the primary absorber was met with an ascending gas stream of stripping H_2 which was intended to be free of HCl and to contain only BCl_3 and DCB, plus a small amount of dissolved H_2 .

The liquid absorber bottoms entered the DCB fractionator and disproportionator at about its midpoint. Fractionation of the DCB from the BCl_3 was supplied by counterflow of gaseous BCl_3 vaporized by an electrical heater in the bottom of the unit versus liquid BCl_3 condensed on the cooling coil in the top of the unit. Dichloroborane then was condensed in the top of the unit and disproportionated into B_2H_6 and BCl_3 . The B_2H_6 gas then was allowed to go out the top together with the H_2 which had entered in the absorber bottoms. The BCl_3 liquid, stripped of DCB and H_2 , left the bottom of the unit and was collected in a BCl_3 receiver. Between runs it could be recycled to the BCl_3 supply cylinder for reuse in the succeeding run.

Details of the prepilot plant flow system and sampling equipment are given in Appendix G.

B. Discussion

1. Operation and Data

The separation steps of the prepilot plant were operated during 25 separate runs, beginning with Run 903.

The measurements and calculations of the basic H_2 and BCl_3 flow rates are presented in Table 46. The basic flow rate calculations are keyed to conform to the chemically determined ratio of H_2 to BCl_3 in the reactor feed in order to make each run calculation internally consistent.

The complete results of chemical and infrared analyses are tabulated in Appendix H. The H_2 and BCl_3 flow rates and chemical compositions for the calculation of material balances are summarized in Table 47. In addition to flow rates which were selected from Table 46, this table also lists the measured flow rates of total overhead gas from the disproportionator. Table 48 presents a summary of the operating factors and material balances for the absorber-disproportionator sections.

The steady state temperatures and pressures for these runs are presented in Tables 49-A and 49-B.

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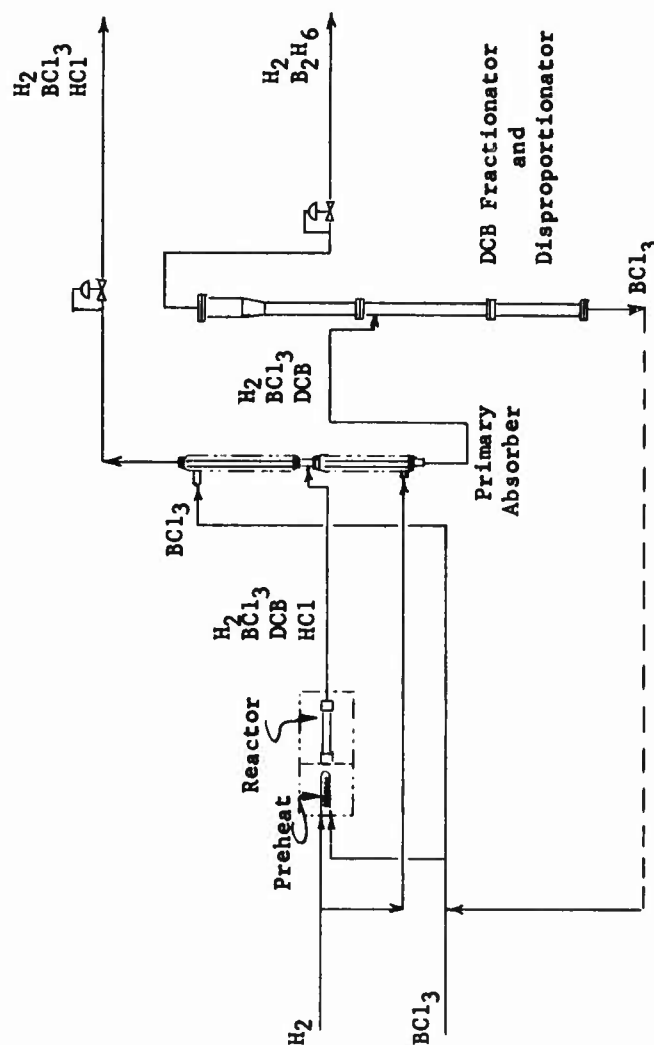


Figure 35. Simple Flow Diagram, Diborane Prepilot Plant

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TABLE 46

SUMMARY OF H_2 AND BCl_3 FLOW RATES

Parenttheses are used to denote H_2 and BCl_3 flow rate values which are considered less reliable either because of known experimental difficulty or because of internal non-consistency with other data and results.

RUN NO.	HYDROGEN FLOW RATES ^(a)				RATIO H ₂ :BCl ₃ to Reactor ^(f)	BCl ₃ FLOW RATES ^(a)				
	H ₂ to Reactor & Absorber ^(b)	H ₂ to Stripper ^(c)	H ₂ to Reactor			BCl ₃ to Reactor & Absorber ^(b)	BCl ₃ to Reactor		BCl ₃ to Absorber Orifice Pressure Drop (psi)	Calc. ⁽ⁱ⁾
			Meas. ^(d)	Calc. ^(e)			Meas. ^(g)	Calc. ^(h)		
903	-	172	650	-	2.82	-	(220)	231	85	(j)
904	753	172	650	(581)	2.72	884	(220)	239	87	645
905	756	172	650	(584)	2.94	956	(220)	221	162	735
906	247	172	(k)	(75)	0.62	861	163	(121)	106	698
907	995	172	610	(823)	3.60	938	(163)	169	105	769
908	569	(172) ^(l)	500	(397)	2.43	903	(196)	206	105	697
1001	-	(172)	221	-	3.48	-	(62)	64	108	-
1002	223	(172)	221	(51)	3.68	759	(62)	60	106	699
1003	235	(172)	221	(63)	3.94	765	(62)	56	105	709
1004	-	(172)	221	-	4.41	769	(62)	50	106	719
1005	-	(172)	215	-	4.30	829	(81)	50	106	779
1101	-	356 ^(m)	215	-	1.67	431	(81)	129	106	302
1102	572	356	219	(216)	2.88	440	(74)	76	105	364
1103	585	356	219	(229)	2.98	769	(74)	74	108	695
1104	211	(n)	219	(211)	2.69	753	(74)	81	108	672
1201A	394	(356) ^(o)	(157) ^(o)	(38) ^(o)	3.32	801	(74) ^(o)	(47) ^(o)	108	(o)
1201B	305	(356) ^(o)	(157) ^(o)	(-51) ^(o)	2.77	801	(74) ^(o)	(50) ^(o)	108	(o)
1202	551	356	(218)	195	3.87	619	(74)	50	108	569
1203	229	(356) ^(p)	(236) ^(p)	(-127) ^(p)	1.74	693	(74) ^(p)	(132) ^(p)	105	(p)
1204	336	142 ⁽ⁱ⁾	(254)	194 ^(q)	0.88	846	(r)	220	108	626
1301	470	172	(296)	298	3.49	693	(83)	85	106	608
1302	801	172	(620)	629	3.36	775	(171)	187	106	588
1303	804	172	(620)	632	3.46	775	(171)	183	108	592
1304A	575	0	(620)	575	2.99	772	(171)	193	102	579
1304B	727	172	(620)	555	2.99	772	(171)	186	102	586
1305	758	172	(620)	586	3.33	781	(171)	176	102	605
1401	747	172	(620)	575	3.39	772	(171)	170	107	602

(s) All flow rates are given in units of 1.0×10^{-4} lb. moles/hr

(b) By cylinder inventory.

(c) Measured by H_2 orifice calibration.

(d) Measured by H_2 flowmeter.

(e) Calculated by cylinder inventory less H_2 to stripper

(f) From data in Table 47

(g) Measured by BCl_3 flowmeter.

(h) H_2 to reactor divided by $H_2:BCl_3$ ratio.

(i) Calculated by cylinder inventory less BCl_3 to reactor.

(j) Run 903: Rate of BCl_3 to absorber was assumed to be the same as that for Run 904, 645×10^{-4} lb. moles per hour

(k) Run 906: Rate of H_2 to reactor was assumed to be equal to. $(BCl_3 \text{ to reactor, measured}) \times (H_2:BCl_3 \text{ ratio}) = 165 \times 10^{-4} \times 0.62 \times 10^{-4}$ lb. moles per hour

(l) Runs 908 through 1005: Rate of H_2 to stripper is believed to have decreased to nearly zero due to plugging of fixed orifice. Evidence includes comparisons which are shown in this Table and in the fact that poor stripping of HCl (see Table 51) from absorber bottoms could not be otherwise explained.

(m) Run 1101: There is no corroboration to be seen of the stated H_2 rate to the stripper. Poor HCl stripping indicates the rate was less than is shown above

(n) Run 1104: The H_2 to stripper orifice is known to have been plugged during this run.

(o) Runs 1201-A and 1201-B: Only the rate figures which were derived directly from H_2 cylinder and BCl_3 cylinder inventory data can be considered reliable in view of internal inconsistencies in data for this run, and in view of known shifts in flowmeter calibrations.

(p) Run 1203: Only the rate figures which were derived directly from H_2 cylinder and BCl_3 cylinder inventory data can be considered reliable because of internal inconsistencies in this run.

(q) Run 1204: The H_2 to stripper orifice appears to have been partially plugged during this run. The rate shown was estimated on the basis of the time which H_2 flow required to pressurize the absorber from 40 to 80 psia at the start of the run. For Run 1204, this was 55.8 seconds, for Run 1301, 46.1 seconds. Hence $(46.1/55.8) \times 172 \times 10^{-4} = 142 \times 10^{-4}$ lb. moles per hour. Run 1204 was the first run for which this measurement was made.

(r) Run 1204: The BCl_3 to reactor flowmeter was found to have been improperly installed; its reading is not reported.

TABLE 47
SUMMARY OF SELECTED FLOW RATES AND CHEMICAL ANALYSES FOR CALCULATION OF MATERIAL BALANCES

RUN NO	RECOMMENDED FLOW RATES (10×10^{-4} lb. moles/hr. unit)				A N A L Y S I S (m o l e p e r c e n t)				A B S O R B E R				D I S P R O P O R T I O N A T E R				D I S P R O P O R T I O N A T E R			
	(from Table 46)				R E A C T O R P R O D U C T (A b s o r b e r F e e d)				A B S O R B E R O V E R H E A D				D I S P R O P O R T I O N A T E R O V E R H E A D				D I S P R O P O R T I O N A T E R B O T T O M S			
	H ₂				B C l ₃				B C l ₃				B C l ₃				B C l ₃			
	To Reactor	To Absorber for stripping	To Reactor	To Absorber for absorption	Total Overhead Gas from Disproportionator	B C l ₃	B H C l ₂	B C l ₃	B C l ₃	B H C l ₂	H ₂ by Difference	H ₂ by Wet Determination	B C l ₃	B H C l ₂	H ₂ by Wet Determination	H ₂ from Non-condensable gases at -196°C	H ₂ by Difference	H ₂ by Wet Determination	B H C l ₂	H ₂ by Difference
903	650	172	231	645		23.4	2.80	24.8	1.28	(2.0)	3.6	70	1.7	4.1	-	-	-	-	-	-
904	650	172	239	645		22.7	4.14	24.5	1.80	(1.2)	2.25	72	3.1	-	-	-	-	-	-	-
905	650	172	221	735		20.8	4.55	26.5	1.32	-	-	69	4.45	8.7	-	-	-	-	14.6	-
906	101	172	163	698		55.4	6.31	15.2	0.0	(0.25)	3.2	76	3.2	7.3	-	26	-	27	8.7	27
907	610	172	169	769		16.9	4.85	20.2	0.90	-	-	76	5.0	-	-	-	-	-	6.0	19
908	500	69(a)	206	697		23.8	5.22	23.1	1.14	(1.3)	5.0	68	5.0	7.7	-	22	-	-	6.0	-
1001	221		64			17.7	4.7													
1002	221	0	60	699	11.1	16.7	4.7	13.3	0.0	-	-	84	3.0	6.0	-	26	-	43	6.0	-
1003	221	0	56	709	11.1	15.6	4.7	10.6	0.0	-	-	86	2.3	6.5	-	27	-	42	6.5	-
1004	221	0	50	719	10.1	14.1	4.4	18.2	0.0	-	-	79	3.0	6.5	-	22	-	(39)	6.5	-
1005	215	0	50	779	5.3	14.4	4.48	16.3	0.0	-	-	81	2.0	0.0	-	40	-	(31)	0.0	-
1101	215	356(b)	129	302	4.8(c)	32.1	5.37	15.1	0.1	-	-	82	5.72	0.0	-	27	-	(18)	0.0	-
1102	219	356	76	364	1.5(c)	20.5	5.26	14.5	1.22	-	-	83	0.0	0.0	-	73	-	(2)	0.0	-
1103	219	356	74	695	2.8	19.8	5.25	14.1	0.25	-	-	83	1.10	0.0	-	26	-	(33)	0.0	-
1104	219	0	81	672	7.4	22.3	4.92	23.3	0.0	(0.16)	4.60	72	1.92	0.0	-	35	-	-	0.0	-
1201A	(d)	(d)	(d)	(d)	3.7	18.2	4.99		0.4	-	-	63	2.56	0.5	-	56	-	(3)	0.5	-
1201B	(d)	(d)	(d)	(d)	3.7	21.6	5.20	34	0.16	-	-	82		0.2	-	72	-	(3)	0.2	-
1202	195	356(e)	50	569	3.0	16.8	4.4	15.3	0.0	-	-	85		0.0	-	40	-	(4)	0.0	-
1203(e)	(e)	(e)	220	626	4.8	33.4	4.8	12.3	0.0	(0.12)	3.3	84		0.2	-	58	-	(4)	0.2	-
1204	194	142				49.0	4.3	12.2	0.0	-	-	85		0.0	-	59	-	(2)	0.0	-
1301	298	172	85	608	3.5	17.3	5.03	12.2	0.0	(0.21)	2.24	86		0.0	-	57	-	(4)	0.0	-
1302	629	172	187	588	3.8	17.4	5.07	11.9	0.48	(0.25)	2.97	85		0.0	-	56	-	(2)	0.0	-
1303	632	172	183	592	3.7	18.2	4.24	11.4	0.17	-	-	86		0.0	-	54	-	(12)	0.0	-
1304A	575	0	193	579	3.9	20.1	4.98	10.6	0.0	-	-	86		0.0	-	55	-	(7)	0.0	-
1304B	555	172	186	586	4.4	20.1	4.98	10.8	0.08	(0.15)	2.24	87		0.0	-	58	-	(1)	0.0	-
1305	586	172	176	605	3.8	18.2	4.92	10.35	0.30	-	-	86		0.0	-	25	-	(4)	0.0	-
1401A	575	172	170	602	8.4(f)	17.65	5.11	11.4	0.08	-	-	86		0.3	-	2.4	-	-	0.3	-
1401B	575	172	170	602	3.8	17.65	5.11	11.4	0.08	-	-	86		0.3	-	0.0	-	-	0.3	-

(a) Run 908: H₂ to absorber for stripping estimated from Table 46 Data. 569×10^{-4} Total H₂ less 500×10^{-4} lb. moles per hour to Reactor.

(b) Run 1101: H₂ to absorber for stripping rate value seems uncertain. (Note "g", Table 46)

(c) Run 1102: The disproportionator pressure rose relatively slowly during this run. The run was discontinued prematurely. The value for product gas rate was calculated on the basis of estimated gas volume in disproportionator: 808 C.F., in which the pressure rose from 24.0 to 34.5 psia in 56 minutes.

(d) Parts A and B of Run 1201: See Note "f", Table 46.

(e) Run 1203: See Note "g", Table 46.

(f) Part B of Run 1401: Total overhead gas rate was assumed to be average of Runs 1302, 1303, 1304A, and 1305, because the rate of disproportionator pressure rise from 60 to 75 psia was 97% of the average of those four runs for the same pressure range. See Figure 18 for pressure rise curves of these runs.

(g) H₂ (by difference) in Absorber overhead was estimated when no HCl analysis was given by assuming that the HCl content was 3.0%.

(h) HCl by wet determination: Total chloride less chloride attributable to BCl₃ and to BHCl₂. BCl₃ and BHCl₂ for this purpose were determined by Infra red analysis.

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TABLE 48
SUMMARY OF OPERATING FACTORS AND MATERIAL BALANCES. COMBINED ABSORBER AND DISPROPORTIONATOR

RUN NO	EQUIPMENT DETAILS AND CONDITIONS					BHC1 ₂ AND HCl MATERIAL BALANCES (c)									
	ABSORBER			DISPROPORTIONATOR		BHC1 ₂ or HCl In React. Prod.	BHC1 ₂ OUTPUT (I. R. BASIS)			HCl OUTPUT					
	Packing (a)	Jacket (b)	Ratio H ₂ Absorb. Bottoms	No. of Plates (c)			Temp. (°F)	Total Press. (psia)	Absorb. Overhd.	Absorb. Bottoms	Disprop. Overhd. (f)	BHC1 ₂ Loss	Absorb. Overhd.	Disprop. Overhd.	HCl Loss
				UPPER	LOWER										
903	SS	A	0.3	10	33	93	24.7	14.5	9.6	-	-	-	40.9	-	<-16.2
904	SS	A	0.3	4	33	93	36.8	19.6	19.2	-	-	-	24.5	-	<-12.3
905	SS	A	0.3	10	33	93	39.6	14.9	28.9	-	-	-	-	-	-
906	SS	Fr	0.2	(4)	33	93	16.7	0.0	25.6	18.0	-	-	10.7	2.7	3.3
907	SS	Fr	0.3	3	33	93	27.8	8.8	-	-	-	-	-	-	-
908	SS	Fr	0.1	2	33	93	36.9	8.9	34.7	28.2	-	-	38.9	1.9	- 3.9
1001															
1002	SS	FrUr	0.0	(4)	33	91	13.4	0.0	22.0	12.7	-	-	-	-	-
1003	SS	FrUr	0.0	(4)	33	91	13.0	0.0	17.2	12.6	0.4	-	-	4.8	-
1004	SS	FeUc	0.0	(4)	33	91	11.9	0.0	21.9	13.1	-1.2	-	-	4.7	-
1005	SS	FeUcLh	0.0	(4)	-89	91	11.9	0.0	15.9	8.5	3.4	-	-	4.5	-
1101	SS	FeUcLh	1.1	inf	-82	89	18.5	0.7	18.9	15.0	2.8	-	-	1.8	-
1102	SS1D	FeUcLh	1.0	2	(g)	34.5	15.5	8.2	0.0	1.8(h) max	5.5+	-	-	1.0	-
1103	SS1D	FeUcLh	0.5	3	-80	91	15.4	1.7	7.4	4.2	9.5	-	-	0.3(h)	-
1104	SS1D	FaUaLa	0.0	(4)	-87	95	14.8	0.0	13.3	14.4	0.4	-	12.9	3.1	- 1.2
1201A	SS1D	FaUaLa			-74	96									
1201B	SS1D	FaUaLa			-74	96									
1202	SS3D	FeUcLc	0.7	4	-94	94	10.8	1.8	16.6	9.1	-	-	-	0.09	-
1203	SS3D	FeUcLc			-84	94.5		1.1	-	4.7	5.0	-	-	0.05	-
1204	SS3D	FeUcLc	0.2	(4)	-102	94.5	17.8	0.0	-	14.1	-	-	-	1.1	-
1301	SS3D	FeUcLc	0.3	(4)	-108	93	19.3	0.0	-	10.7	7.1	-	12.4	0.2	5.2
1302	SS3D	FeUcLc	0.3	4	-96	94	41.4	4.7	-	8.4	10.9	-	-	0.03	-
1303	SG3D	FeUcLc	0.3	4	-99	94	34.6	1.5	-	9.8	26.9	-	22.3	0.02	19.1
1304A	SG3D	FeUcLc	0.0	(4)	-99	94	38.2	0.0	-	9.3	23.8	-	26.8	0.10	7.7
1304B	SG3D	FeUcLc	0.2	5	-99	94	36.9	0.6	-	6.9	31.3	-	-	0.6	-
1305	SS	FeUcLc	0.2	3	-103	93	37.5	2.5	43.8	9.2	25.8	-	18.5	0.06	18.9
1401A	SS	FeUcLc	0.2	6	-103	35	38.1	0.7	35.6	36.7	0.7	-	-	0.2	-
1401B	SS	FeUcLc	0.2	6	-103	75	38.1	0.7	35.6	11.4	26.0	-	-	-	-

(a) Internal packing schemes SS = stainless steel, protruded; "Canon," 0.16" packing in both upper and lower sections of absorber. SG = stainless steel, protruded; "Canon," 0.16" packing in upper section of absorber and 3 mm glass spheres in lower section of absorber.

ID = Single redistributor on top of packing, lower section

3D = Two redistributors in lower section, one redistributor at mid height of packing, upper section.

(b) External jacketing schemes.

A = No jacketing; all exterior surface exposed to ambient temperature

F = BCl₃ feed pipe and top of absorber jacketed, using cooling water.

FU = Same as F with upper section of absorber also jacketed.

FUL = BCl₃ feed, upper section, and lower section, all jacketed.

r = Refrigerated water in coil.

c = City water in coil (52°F in Run 1004 to 34°F in Run 1401).

h = Hot water in coil (approx. 120°F).

a = Recirculated water, heated to ambient temperature, in coil

Upper Section - BHC1₂ Removal Lower Section - HCl Removal

(c) Indicated number of theoretical plates

(°F)

(d) Temperature - Coolant into condenser

(e) The disproportionation reaction temperature was not measured, but it was probably about the same as for Run 1103, namely -80°F.

(f) Disproportionation Overhead - BHC1₂ + 6 x BzH₆

(g) Run 1102 The estimated maximum non H₂ content of the Disproportionate gas was 0.3 x 10⁻⁴ lb moles per hour. Conceivably this was either all HCl or all BzH₆

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TABLE 49 - A
STEADY STATE TEMPERATURES AND PRESSURES

RUN NO.	903	904	905	906	907	908	1001	1002	1003	1004
REACTOR & ABSORBER MEASUREMENTS										
Temperature (°F)			(a)							
Reactor Inlet Temp. (T ₁)	1275-1312	1292-1315	1300-1304	1277-1300	1300-1303	1298-1302	1297	1300-1303	1299-1302	1299-1302
Reactor Discharge Temp.	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300
Quick Quench Exit Temp. (T ₃)	124	122	113	95	94	97	65	66	67	64
Absorber Inlet Gas Temp. (T ₄)	89	76	81	85	77	80	65	71	70	67
Absorber Skin Temp. (T ₅) 2' Above Feed	68	65	62	79	59	72				
Opposite Feed ^(b)							53	48	52	55
Absorbent BCl ₃ Feed Temp.	-	-	-	37	34	36	-	35	33	52
Pressure (psia)										
H ₂ Feed (P ₂)	279	279	279	279	279	279	279	279	279	279
BCl ₃ Feed (P ₃)	188	190	265	210	210	210	210	210	210	210
Quench Exhaust Gas (P ₄)	103	103	103	105	105	105	101	105	105	104
Absorber Top Gas (P ₆)	103	103	103	104	105	105	102	104	105	104
DISPROPORTIONATER MEASUREMENTS										
Top Pressure (P ₇)	93	93	93	93	93	93	-	91	91	91
Bottoms Temp. (T ₂)	162	162	162	157	162	157	-	159	160	160
Indic. Top Gas Temp. ^(c) (T ₈)	47	43	43	42	41	46	-	42	42	41
BCl₃ RECEIVER										
Pressure (psia) (P ₅)	30	20	22	35	39	-	-	-	-	-

(a) The reactor inlet temperature dropped during Run 906. To counteract this, the heat input to the preheat furnace was progressively increased, raising the preheat atmosphere to 1580°F. Note that this situation may be expected at low ratio H₂:BCl₃ in reactor feed.

(b) T₆ was lowered to a point opposite absorber feed before Run 1001. Its previous location was covered when all the top section was covered with cooling coils.

(c) The indicated disproportionater temperature was influenced by radiation from the unjacketed head of the disproportionater.

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C O N F I D E N T I A L

T A B L E 49 - B
S T E A D Y S T A T E T E M P E R A T U R E S A N D P R E S S U R E S

RUN NO	1005	1101	1102	1103	1104	1201	1202	1203	1204	1301	1302	1303	1304	1305	1401
REACTOR ABSORBER MEASUREMENTS															
Temperature (°F)															
Reactor Inlet Temp.	1300	1300	1300	1300	1300	1300	1300	1300	1240-1300	1300	1300	1300	1300	1300	1300
Reactor Discharge Temp.	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300
Quick Quench Exit Temp	61	70	-	58-66	60-64	63	70	74	95	56	65	63	66	66	83
Absorber Inlet Gas Temp.	70-74	72-75	65-66	68-70	67-72	71	73	73	75	70	68	68	65	66	68
Absorbent BCl ₃ Temp.	-	45-46	42-43	41-45	70(est.)	70	50	43	41	37	37	34	33	33	34
Absorber Skin Temp.	60-62	73-80	98-100	94-97	68-72	70	59	71	70	56	58	60	66	65	62
Absorb. Low Sect. Heating Coil Temp.	116-122	118-126	115-118	117-125	70(a)	-	-	-	-	-	-	-	-	-	-
Absorb. Low Sect. Cooling Coil Temp.	-	-	-	-	-	85	50	42	40	35	37	35	33	36	34
Pressure (psia)															
H ₂ Feed Pressure	280	280-285	280	280	280-281	280	280	280	280	280	280	280	280	280	280
BCl ₃ Feed Pressure	210	210	210	210-211	210	210	210	208	210	210	210	210	210	210	210
Reactor & Tubing Pressure Drop	0	3	3	3	3	3.5	3	4	7-13	0	3	3.4	2	2	2
Quench Exhaust Gas Pressure	104	105	105	102	101-102	101	101	102	101	102	102	100	107	106	108
Absorber Top Gas Pressure	104	104	105	102	101-102	102	102	103	102	103.5	103.5	102	108	108	103
DISPROPORTIONATER MEASUREMENTS															
Top Pressure (b)	91	89	(c) 34.5	91	95	96	94	94.5	94.5	93	94	94	94	93	75
Boiler Temp. (b)	155	152	88(c)	155	155	152	157	160	159	156	(155)	156	155	153	89
Coolant to Condenser Temp	-89	-82	-	-80	-87	-74	-94	-84	-102	-108	-96	-99	-99	-103	-103
Coolant from Condenser Temp	-81 to -85	-77	-	-77	-80	-67	-86	-80	-96	-103	-92	-94	-92	-96	-94
Indicated Top Gas Temp	-69 to 71	-66 to -69	-	-50 to 70	-66 to -68	-66	-79	-75	-80	-92	-74	-83	-82	-80	-79

(a) Jacket temperature rose during Run 1104 from 64°F to 73°F. Its value was 70°F during period of product gas withdrawal.
(b) During pressurization period, while disproportionator contents were at constant reflux, the boiler pressure-temperature relationship for Runs 1005, 1101, 1102, 1103 and 1104 was closely approximated by: $\log_{10} \text{mp} = 7.4094 - 1273.6/T(^{\circ}\text{K})$ over the temperature range 70°F to 160°F.
(c) Maximum: Run 1102 was terminated before disproportionator reached full pressure.
(d) During Run 1103, the disproportionator top gas temperature rose to -50°F when dry ice in coolant was nearly exhausted. This occurred at 193 minutes during a sampling of the disproportionator overhead gas sample.
(e) The value, -98°F, is lower than that of the coolant leaving condenser at the top of the disproportionator. Possible explanation is that no gas was leaving at the time

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The three principal process steps were operated smoothly from the offset of their integration in Run 903. No difficulties were encountered in sustaining uniform and reproducible conversion to BHCl_2 in the hydrogenator, separation of BHCl_2 from H_2 and HCl in the absorber, and segregation of the BHCl_2 and disproportionation to B_2H_6 in the disproportionator.

The problems in this investigation all proved to be problems in evaluation of the performance of the integrated process system. In the latter part of this investigation, these were resolved as having been caused by nearly complete plugging of fixed orifices of small diameter, and by condensation and resultant trapping of a major portion of the product B_2H_6 in the condenser section of the disproportionator. Because the almost complete plugging of the fixed orifice in the stripping H_2 line in Runs 908 through 1101 was not immediately apparent, other possible explanations for the high HCl content of the product gas were at first sought. Similarly, other explanations of the apparent loss in B_2H_6 yield, including possible back reactions, were sought when, in fact, trapping of B_2H_6 in the condenser was the cause.

Solution of these problems was obscured until perfection of concurrent auxiliary flow measurements gave a positive confirmation and cross-check of the material balance flow rates. The flow rates which were thus made better known were total H_2 , total BCl_3 , and relative rate of filling of the disproportionator. A second overhaul of the H_2 and of the BCl_3 flowmeters increased the reproducibility of flow rates. Doubling of reactor feed rates, beginning with Run 1302, enabled the apparent loss in yield of B_2H_6 to be more clearly defined.

2. Performance of Absorber

a. BHCl_2 Absorption

The performance of the absorber in separating BHCl_2 from the H_2 and HCl in the overhead gas can best be measured by calculating the number of theoretical equilibrium plates which would be required to effect the same operation. For the purpose of making such calculations chemical engineering texts supply the formula:

$$(\text{fraction unabsorbed}) = \frac{(\text{absorption factor}) - 1}{(\text{absorption factor})^N + 1 - 1}$$

as applicable whenever both the operating and the equilibrium lines may be assumed to be straight. The "absorption factor", $\frac{L}{KV}$, is seen to be a ratio of the slope of the operating line, $\frac{L}{V}$, to the slope of the equilibrium line, K . The letter, N , is the number of theoretical equilibrium plates employed. For simplicity in setting up Figure 36 from the data of Table 50, the approximation was made that the mole per cent of BHCl_2 in the vapor stream

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entering the absorber section was about the same as the mole per cent of BHCl_2 in the absorber feed, namely about 5.0 per cent. Hence, the formula:

$$(\% \text{ BHCl}_2) \text{ in off-gas} = 5.0 \times \frac{\left(\frac{L}{KV}\right)^N - 1}{\left(\frac{L}{KV}\right)^{N+1} - 1}$$

The calculated values of K were adjusted for temperature by reference to the vapor pressure of BCl_3 as shown by its mole fraction of absorber overhead gas.

In Figure 36, 13 of the 14 significant points can be said to cluster about the line drawn for four theoretical equilibrium plates. The fourteenth point, for Run 1101, which is in poorest agreement, is based on less certain data for stripping H_2 rate, as is mentioned in Tables 46 and 47. The ten analyses in which 0.00 per cent BHCl_2 was reported are not sufficiently definitive to be helpful in this evaluation of absorber performance.

The calculated height equivalent to a theoretical plate (H.E.T.P.), based on 21 inches of the protruded 0.16 x 0.16 inch Cannon type packing, then becomes about 5 inches for the system BCl_3 - BHCl_2 . This is believed to be a reasonable value, being from two to three times the value which the suppliers of this packing report for selected hydrocarbon systems.

b. HCl Stripper

By a mathematical method which is analogous to that described above the absorbing section of the absorber, chemical engineering texts derive the formula:

$$(\text{fraction not stripped}) = \frac{(\text{stripping factor}) - 1}{(\text{stripping factor})^{N+1} - 1}$$

for the stripping section. In this formula, the stripping factor, $\frac{KV}{L}$, is seen to be the inverse of the "absorption factor", $\frac{L}{KV}$. It is the ratio of the slope of the equilibrium line, which is assumed to be straight, to the slope of the operating line, which is likewise assumed to be straight.

Figure 37 was established from the data of Table 51 with the assumption of a uniform value for the concentration of HCl in the liquid stream entering the stripping section. A proper value for this would be the same concentration which would occur if no stripping H_2 were employed. Reference to the calculated results for Runs 1002 through 1005, and Run 1104 in Table 51 shows that these were in the range 2200 to 6500 parts HCl per million parts liquid on a mole basis, depending somewhat on

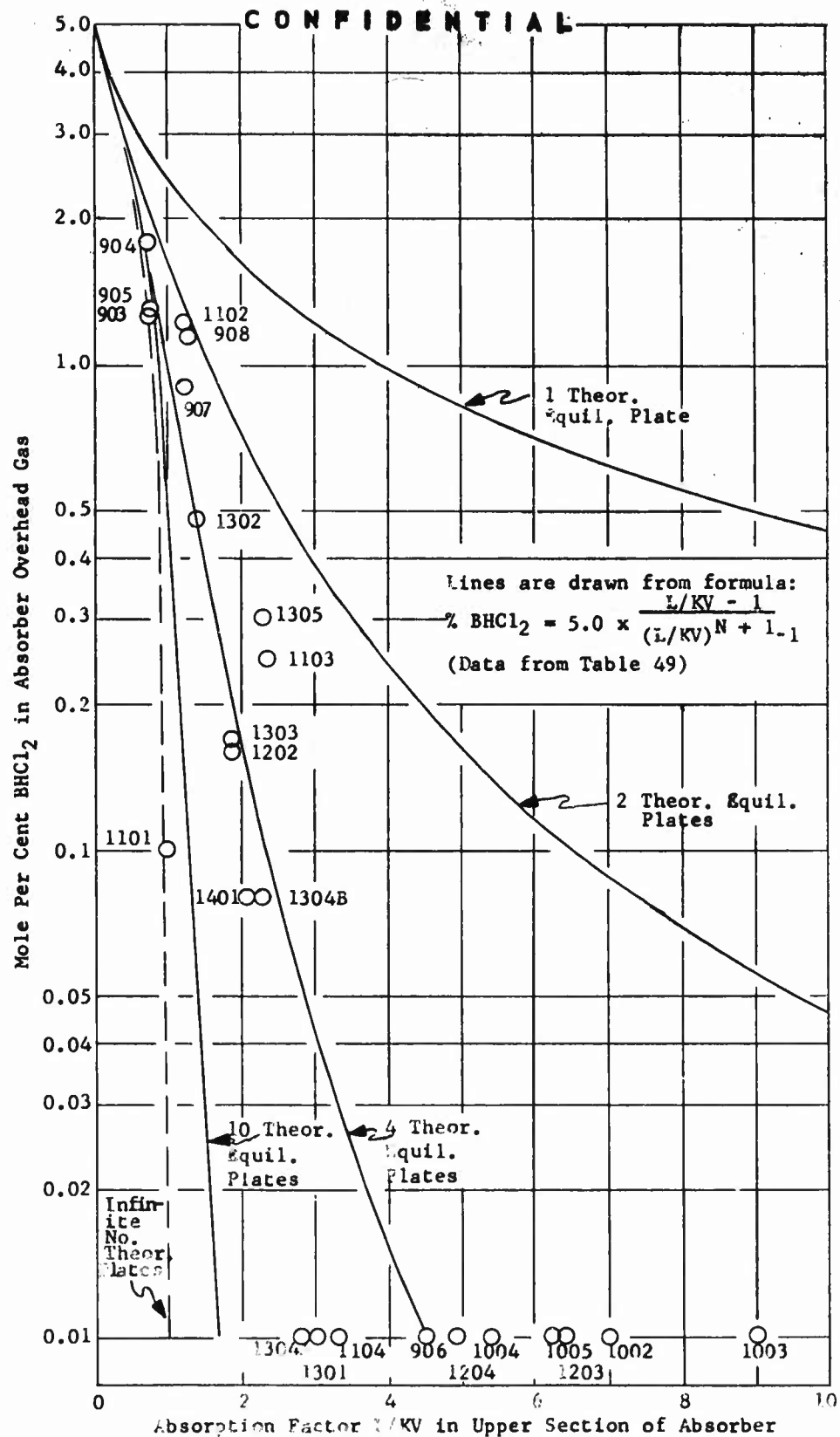


Figure 36. Absorption of BHC1_2 in Absorber

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TABLE 50
DATA AND CALCULATION SUMMARY: BHCl_2 ABSORPTION IN ABSORBER UPPER SECTION(a)

RUN NO	H ₂ FLOW RATES			UPPER SECTION FLOW RATES		UPPER SECTION PERFORMANCE			
	TOTAL H ₂ TO REACT & ABSORB	CALCULATION		H ₂ IN ABSORB. OVERHD. GAS (b)	ABSORB. OVERHD. GAS (c)	BCl ₃ ABSORB. RATE	CALCULATION SOL. CONSTANT $\frac{K}{\text{for } \text{BHCl}_2}$ (d)	ABSORPTION FACTOR FOR $\frac{\text{L}}{\text{KV}}$	BHCl ₂ IN ABSORB. OVERHD. GAS (%)
		H ₂ & BCl ₃ to Reactor	BHCl ₂ in Absorb. Feed						
903	822	881	25	795	1136	645	0.77	0.74	1.28
904	822	889	37	782	1087	645	0.76	0.77	1.80
905	822	871	40	779	1129	735	0.82	0.79	1.32
906	273	264	17	254	334	698	0.47	4.4	0.0
907	782	779	38	742	977	769	0.63	1.25	0.90
908	569	706	37	530	779	697	0.72	1.24	1.14
1001		285	13						
1002	221	281	13	206	245	699	0.41	7.0	0.0
1003	221	277	13	206	239	709	0.33	9.0	0.0
1004	221	271	12	207	262	719	0.56	4.9	0.0
1005	215	265	12	201	248	779	0.50	6.3	0.0
1101	571	344	18	551	671	302	0.47	0.96	0.1
1102	575	295	16	557	671	364	0.45	1.20	1.22
1103	575	293	15	558	673	695	0.44	2.35	0.25
1104	219	300	15	202	281	672	0.72	3.3	0.0
1201A	394								
1201B	305				460				0.4
1202	551	245	11	538	656	569	0.47	1.84	0.16
1203	229		15(c)	214	251	600	0.38	6.3	0.0
1204	336	414	18	316	376	626	0.38	4.4	0.0
1301	470	383	19	449	529	608	0.38	3.0	0.0
1302	801	816	41	858	997	588	0.37	1.59	0.48
1303	804	815	35	767	903	592	0.35	1.88	0.17
1304A	575	768	38	555	623	579	0.33	2.8	0.0
1304B	727	741	37	688	800	586	0.33	2.22	0.08
1305	758	762	38	718	825	605	0.32	2.29	0.30
1401A	747	745	38	707	822	602	0.35	2.09	0.08
1401B	747	745	38	707	822	602	0.35	2.09	0.08

- (a) All flowrates are given in units of 1.0×10^{-4} lb. moles/hr.
 (b) In calculation of H₂ in absorber overhead gas, assume that 2×10^{-4} lb. moles H₂ per hour are dissolved in absorber bottoms.
 (c) To calculate total absorber overhead gas, divide total H₂ in absorber overhead gas by per cent H₂ (from Table 47).
 (d) Basis for calculation of "K" for BHCl_2 where $K = Y/X$: Note that "K" for BHCl_2 is approximately 3.1 times "K" for BCl_3 at any temperature in this range, and at the same pressure. Note that "K" for any run = percent BCl_3 in overhead gas plus 100.
 (e) Run 1203: The BHCl_2 content of absorber feed was arbitrarily assumed to be 15×10^{-4} lb. moles/hr.

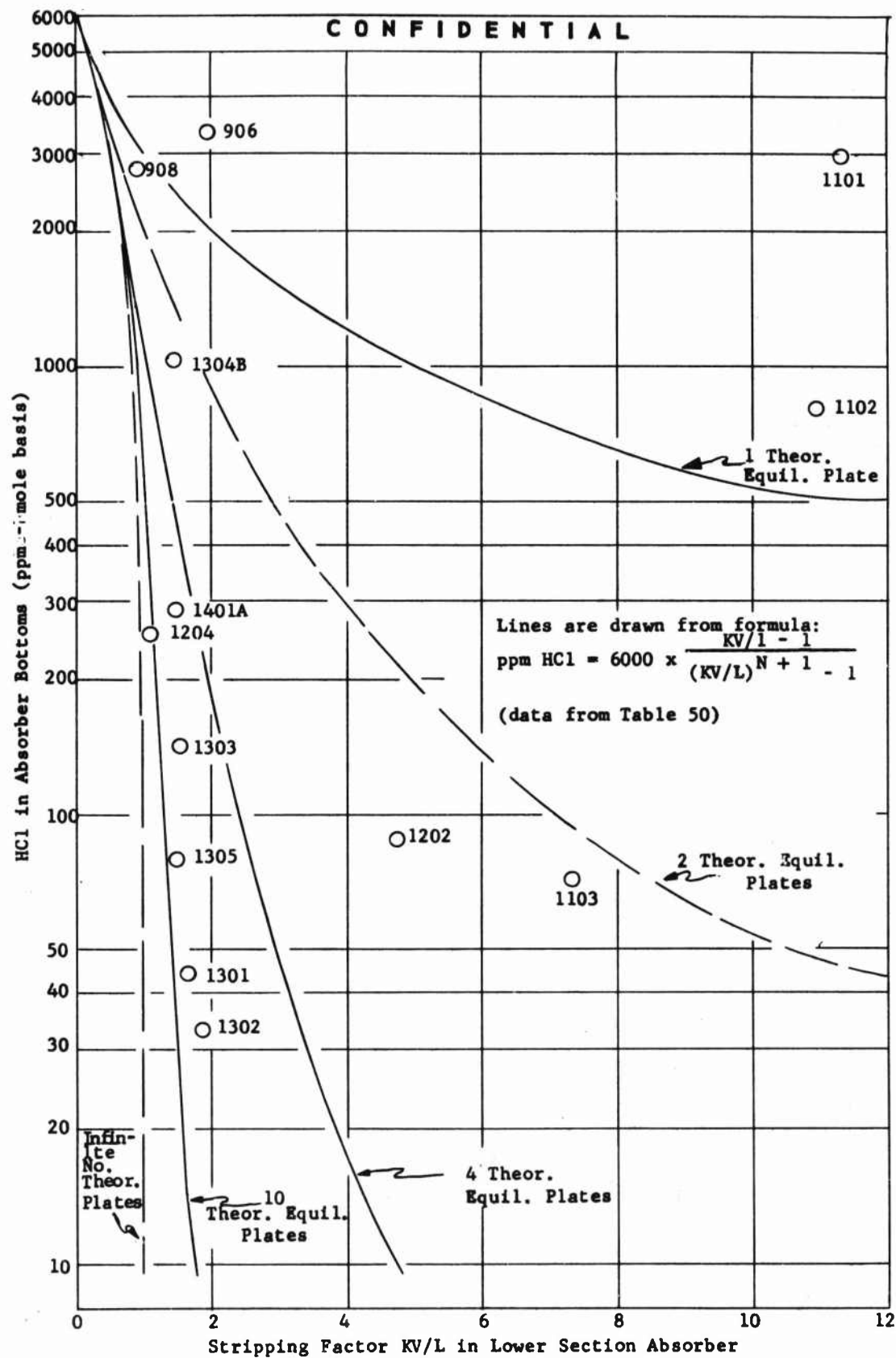


Figure 37. Stripping of HCl in Absorber

TABLE 51
DATA AND CALCULATION SUMMARY: STRIPPING OF HCl IN ABSORBER LOWER SECTION (a)

RUN NO.	CALC. TOTAL MOLES ABSORB. BOTTOMS		CALCULATED VAPOR RATE IN LOWER SECTION			CALC. LIQ. RATE IN LOWER SECTION $\frac{\text{cu. ft.}}{\text{hr.}}$	CALC. SOL. CONSTANT HCl (d)	HCl STRIP. FACTOR $\frac{\text{KV}}{\text{L}}$	CALCULATED APPARENT HCl IN ABSORB. BTMS.		
									Overhd. Gas from Disproportionater		
	H ₂ & BCl ₃ to Reactor & Absorb.	Moles Absorb. Btms. (b)	Ship. H ₂ Rate	Jacket Temp. (°F)	Fugacity BCl ₃ at Temp. (atm)	Total Vapor Rate "V" (°F)			moles	% HCl	HCl Rate
903	1698	562	172	amb	1.34	212	7.57	2.07	-	-	-
904	1706	619	172	amb	1.34	212	7.57	1.93	-	-	-
905	1778	649	172	amb	1.34	212	7.57	1.86	-	-	-
906	1134	800	172	amb	1.34	212	7.57	1.91	9.9(e)	27	2.67
907	1643	666	172	amb	1.34	212	7.57	1.83	-	-	-
908	1472	693	69	amb	1.34	85	7.57	0.90	10.1(e)	19	1.92
1001	-	-	-	amb	-	-	-	-	-	-	-
1002	980	735	0	amb	-	0	-	0.0	-	-	-
1003	986	747	0	amb	-	0	-	0.0	11.1	43	4.77
1004	990	728	0	amb	-	0	-	0.0	11.1	42	4.67
1005	1044	796	0	119	-	0	-	0.0	10.1	44.5	4.49
1101	1002	331	356	122	3.20	653	10.9	11.3	5.3	33.3	1.77
1102	1015	344	356	117	3.03	625	10.7	10.9	4.8	20.4	0.98
1103	1344	671	356	121	3.15	645	10.9	7.3	1.5(f)	-	0.3 (f)
1104	972	691	0	70	-	0	-	0.0	2.8	1.7	0.048
1201A	1195	-	-	85	-	-	-	-	7.4	41.2	3.05
1201B	1106	646	-	85	-	-	-	-	-	-	-
1202	1170	514	356	50	0.92	410	6.48	4.7	3.7	2.5	0.093
1203	922	671	-	42	0.76	-	6.0	-	3.0	1.5	0.045
1204	1182	806	142	40	0.72	158	5.86	1.13	5.8	19.0	1.103
1301	1163	634	172	35	0.65	190	5.61	-	4.8	4.2	0.202
1302	1576	579	172	37	0.67	190	5.72	1.64	3.5	0.8	0.028
1303	1579	676	172	35	-	190	5.61	1.54	3.8	0.5	0.019
1304A	1347	724	0	33	-	0	-	0.0	3.7	2.6	0.096
1304B	1499	699	172	38	0.64	189	5.51	1.45	3.9	16.5	0.64
1305	1539	714	172	36	0.66	190	5.66	1.47	4.4	16.3	0.72
1401A	1519	697	172	34	0.64	189	5.56	1.47	3.8	1.5	0.057
1401B	1519	697	172	34	0.64	189	5.56	1.47	8.4	2.4	0.20
									3.8	-	-

(a) All flowrates are given in units of 1.0×10^{-4} lb. moles/hr.
(b) Total moles absorber bottoms = total moles to reactor and absorber less total absorber overhead gas (from Table 50).
(c) Temperature of jacket, when ambient, was assumed to be 70 °F.
(d) Solubility constant for HCl: "K" is: $K = \frac{y}{x}$ where F is fugacity of HCl

at stated temperature and TT is total pressure. Average value of TT for these runs was 103.5 psia.

(e) Runs 906 and 908: Total moles overhead gas from disproportionater were estimated by dividing H₂ content of gas by assumed H₂ rate. H₂ rate was estimated as 3.5×10^{-3} moles per moles absorber bottoms.

(f) Run 1102: Maximum HCl rate in disproportionater overhead gas was total moles less estimated H₂ rate. Estimated H₂ rate was 1.2×10^{-4} lb. moles per hour.

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the temperature to which the walls of the lower section were heated. The value of 6000 was chosen; hence the formula:

$$\text{ppm HCl (mole basis)} = 6000 \times \frac{\left(\frac{KV}{L}\right) - 1}{\left(\frac{KV}{L}\right)^{N+1} - 1}$$

The plot of results in Figure 37 shows less consistent performance of the packing with respect to stripping HCl in the lower section than Figure 36 shows with respect to packing performance in absorbing BHCl_2 in the upper section. However, all of these deviations may be explained as being due to one or more of the following causes:

(1) Wrong choice of HCl content in liquid stream entering lower section. Thus, if the true value were only 3000 ppm, the lines for each "number of theoretical plates" would be at one-half the indicated ppm HCl for each value of $\frac{KV}{L}$.

(2) Wrong data as to flow rate of stripping H_2 . Thus, if in fact Run 1101 had only 0 to 5 per cent as much stripping H_2 as is shown, its stripping factor, $\frac{KV}{L}$, would be reduced proportionately, and the high HCl in the bottoms during Run 1101 would be better explained.

(3) Too low a value for ppm HCl in bottoms liquid. This value was calculated for each run from analytical data on the sample of off-gas from the disproportionator. These samples have been shown to be not representative to the total B_2H_6 -forming component which entered the disproportionator because of condensation and trapping of a B_2H_6 -HCl mixture on the condenser surface within the disproportionator. Choosing Runs 1302, 1303 and 1305 as examples to show how much the calculated values of ppm HCl could be altered by this correction, Table 48 indicates that for these three runs an average of 25×10^{-4} lb. moles of BHCl_2 -equivalent failed to go out in the disproportionator overhead for each 9×10^{-4} lb. moles which did. On this basis, the true HCl output should likewise have been 3.8 times higher than shown and the ppm HCl in absorber bottoms should be increased to 126 ppm for Run 1302, to 540 ppm for Run 1303, and to 304 ppm for Run 1305.

From the sources of error listed above, it is clear that these data can be only roughly correlated in terms of number of theoretical plates. It appears that most would then fall in the range 2 to 6 theoretical equilibrium plates if the calculated data were more reliable. Since the total height of packing in the lower section was 15 inches, a H.E.T.P. value of between 2.5 inches and 7.5 inches for the stripping of HCl from BHCl_2 would be calculated.

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c. Hydrogen Solubility

The calculated values for dissolved H_2 in the absorber bottoms, which are given in Table 52, may be used to gauge the general agreement between the calculated flow rates of absorber bottoms and the measured flow rate time (% H_2) in the disproportionator overhead gas. For the stated temperature range of Table 52, 34°F. to 122°F., National Distillers and Chemical Corporation workers reported fugacities of H_2 over BCl_3 equal to 2150 to 1590 atmospheres, respectively. According to their data the dissolved H_2 at 34°F. and 7.05 atmospheres would be 3.3×10^{-3} moles per mole absorber bottom, whereas at 122°F., the value would be 4.4×10^{-3} .

The average value for the eight data points shown for Runs 1301 through 1401B in the temperature range 33°F. to 37°F. is 3.15×10^{-3} and the average deviation from this is 0.18×10^{-3} . This seems to be substantiation of the stated good reproducibility and the accuracy of the material balances in these runs.

d. Back Reaction of $BHCl_2$ + HCl in the Absorber

Runs 1102 and 1103 are unique with respect to the conditions in the lower section of the absorber during their progress. For each of these runs, the jacket around the lower absorber section was heated to about 120°F., and H_2 was definitely supplied for stripping.

This probably had the unintended effect of stripping much of the $BHCl_2$ as well as the HCl from the absorber liquid bottoms. As a result, a greater than ordinary concentration of $BHCl_2$ was required in the middle and upper parts of the absorber before the $BHCl_2$ could issue in the bottoms liquid at the concentrations dictated by over-all material balance.

It appears, then, that only in Runs 1102 and 1103 was there an important $BHCl_2$ concentration in the upper section of the absorber, in which the HCl concentration was also relatively high. Thus, some back reaction could have occurred which would in part at least explain the apparent diborane loss for these runs which will be discussed later. It is concluded, therefore, that the temperature of the lower absorber section should be kept substantially below 120°F.

3. Performance of Disproportionator

a. Residence Time for $BHCl_2$

The residence time for $BHCl_2$ within the disproportionator was evidently adequate for the maximum rate at which $BHCl_2$ was supplied to it. If it had not been adequate, there would have been a continuing build-up of $BHCl_2$ content within the distillation column. This would have:

- (1) Caused the product rate to increase during the relatively long period during which it was being measured.

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TABLE 52
Data and Calculation Summary: Dissolved H₂ in Absorber Bottoms
(All flow rates are in units = 1.0×10^{-4} lb. moles per hour)

Run No.	Absorber Conditions		Absorber Bottoms Flowrate	H ₂ in Disproportionator Overhead		Ratio: H ₂ in Disproportionator Overhead to Total Moles Absorber Bottoms
	Stripping H ₂ Rate	Temp. Absorber Bottom (°F.)		Flowrate Total Overhead Gas from Disproportionator	H ₂ Rate in Overhead Gas from Disproportionator	
906	172		800	-	-	-
908	69		693	-	-	-
1002	0		735	11.1	2.9	4.0×10^{-3}
1003	0		747	11.1	3.0	4.0×10^{-3}
1004	0		728	10.1	2.2	3.0×10^{-3}
1005	0	119	796	5.3	2.1	2.6×10^{-3}
1101	356	122	331	4.8	1.3	3.9×10^{-3}
1102	356	117	344	1.5	-	4.4×10^{-3}
1103	356	121	671	2.8	2.0	3.0×10^{-3}
1104	0	70	691	7.4	1.9	2.8×10^{-3}
1201B	-	85	646	3.7	2.1	3.3×10^{-3}
1202	356	50	514	3.0	2.2	4.3×10^{-3}
1203	-	42	671	5.8	2.3	3.4×10^{-3}
1204	142	40	806	4.8	2.8	3.5×10^{-3}
1301	172	35	634	3.5	2.1	3.3×10^{-3}
1302	172	37	579	3.8	2.2	3.8×10^{-3}
1303	172	35	676	3.7	2.1	3.1×10^{-3}
1304A	0	33	724	3.9	2.1	2.9×10^{-3}
1304B	172	33	699	4.4	2.4	3.4×10^{-3}
1305	172	36	714	3.8	2.2	3.1×10^{-3}
1401A	172	34	697	8.4	2.1	3.0×10^{-3}
1401B	172	34	697	3.8	1.8	2.6×10^{-3}

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- (2) Caused the BHCl_2 content of the disproportionator bottoms liquid to rise.

The total residence time of BHCl_2 within the disproportionator was estimated as follows:

- (1) Total liquid hold-up:

$\frac{48}{36} \times \left(\frac{2}{1}\right)^2 \times 2$ cubic inches hold-up in absorber = 10.7 cubic inches hold-up in disproportionator which is about 44×10^{-4} lb. moles as BCl_3 liquid.

- (2) Total vapor hold-up in distillation section:

$52 \times 2^2 \times \frac{\pi}{4} \times 0.85 = 139$ cubic inches vapor, which is about 11×10^{-4} lb. moles as BCl_3 vapor.

- (3) Rectification above feed at essentially total reflux:

18 inches at 4.5 inches H.E.T.P., or 4 theoretical equivalent plates. Relative volatility, BHCl_2 vs. BCl_3 , $\alpha = 3$. BHCl_2 concentration in liquid at feed point:

$$\frac{38}{700} = 0.054$$

Fenske equations for total reflux:

$$\left(\frac{x_{\text{BHCl}_2}}{x_{\text{BCl}_3}}\right)_{\text{Top}} = (\alpha)^4 \left(\frac{x_{\text{BHCl}_2}}{x_{\text{BCl}_3}}\right)_{\text{Feed}}$$

$$= (3)^4 \left(\frac{0.054}{0.946}\right)$$

$$\left(\frac{x_{\text{BHCl}_2}}{x_{\text{BCl}_3}}\right)_{\text{Top}} = \frac{0.822}{0.178}$$

That is, if no disproportionation of BHCl_2 occurred, the concentration of BHCl_2 in the liquid at the top of the tower would be 0.822 mole fraction.

- (4) Average concentration BHCl_2 in section above feed (by applying Fenske equation for one, two, three, and four theoretical equilibrium plate levels):

about 0.40 mole fraction.

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(5) Total BHC1_2 hold-up (maximum, assuming no disproportionation):

$$0.40 \times \left(\frac{18}{48} \times 44 \times 10^{-4} + \frac{18}{52} \times 11 \times 10^{-4} \right) = 8 \times 10^{-4} \text{ lb. moles.}$$

(6) Maximum BHC1_2 residence time:

$$\frac{8 \times 10^{-4}}{38 \times 10^{-4}} = 0.21 \text{ hours, or 13 minutes.}$$

b. Removal of BHC1_2 from Disproportionator Liquid Bottoms

Based on an estimated 4.5 inch H.E.T.P. for the packing, the 30 inch stripping section of the disproportionator below the feed point contained 6.7 theoretical equilibrium plates. The liquid phase concentrations of BHC1_2 were then reduced from $X_F = 0.054$ in the feed to

$$X_B = 0.054 \times \frac{(\text{stripping factor}) - 1}{(\text{stripping factor})^{N+1} - 1}$$

in the bottoms.

Evaluating the stripping factor, $\frac{KV}{L}$:

$$K_{\text{BHC1}_2} = 3 \text{ (inasmuch as tower temperature and pressure are always such as to make } K_{\text{BHC1}_3} = 1)$$

$$V \text{ (at 630 watts input, and } 3.34 \times 10^{-4} \text{ lb. moles per watt-hour)} = 2110 \times 10^{-4} \text{ lb. moles per hour.}$$

$$L = V + \text{Feed (liquid)} = (2110 + 700) \times 10^{-4} \text{ lb. moles per hour.}$$

$$\frac{KV}{L} = 2.2$$

$$X_B = 0.00015$$

The only significant measurement of the BHC1_2 content of the disproportionator bottoms liquid may be the "wet" method value for Run 1303, 0.16 mole per cent, or 0.0016 mole fraction.

At most, the BHC1_2 lost in the bottoms would be about $0.0016 \times 700 \times 10^{-4} = 1.1 \times 10^{-4}$ lb. moles per hour, probably less than the limits of detection in this program.

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c. Explanation of Apparent Losses in Yield of B₂H₆

The fact that the apparent loss in yield of B₂H₆ in the disproportionator was associated with condenser temperature was hinted at by the unexpectedly rapid increase in rate of product gas flow near the conclusion of Run 1302 when the coolant flow to the disproportionator condenser was stopped due to the loss of prime of the circulating pump.

The fact that the apparent loss in yield of B₂H₆ in the disproportionator was associated with disproportionator total pressure was indicated by the graphical plots of rate of filling of the disproportionator during Runs 1302 through 1305. These plots, which appear in Figure 38, show that the rate of filling decreased markedly in each run, when the total pressure passed through the pressure range 50 to 70 psi absolute. The effect of total pressure on apparent yield was clearly established in the two parts of Run 1401 when essentially complete B₂H₆ recovery was obtained at 35 psia but not at 75 psia.

The explanation of these effects of the temperature of the disproportionator condenser and of the total pressure in the disproportionator on the apparent loss in yield of diborane is that:

The temperature of the disproportionator condenser was lower than the dew point of the combined B₂H₆ and HCl content of the total product during those runs for which there was apparent loss in B₂H₆ yield.

This is seen with reference to Figure 39, which is a plot of the vapor pressure of B₂H₆ versus the temperature of the inlet coolant to the disproportionator condenser. For eleven runs, the calculated sum of partial pressures of B₂H₆ and HCl was approximately equal to the vapor pressure of B₂H₆ at the temperature of the inlet coolant. These were Runs 1005, 1101, 1203, 1204, 1301, 1302, 1303, 1304A, 1304B, 1305 and 1401B.

For one run, Run 1104, the calculated sum of partial pressures of B₂H₆ and HCl was higher than the B₂H₆ vapor pressure curve and for four runs, Runs 1103, 1201B, 1202, and 1401A, the calculated sum of the partial pressures of B₂H₆ and HCl was lower than the B₂H₆ vapor pressure curve.

Significant material balances are given in Table 48 on 14 runs in which the results could be influenced by using condenser coolant in the temperature range -74°F. to -108°F. Of these, only three material balances, namely those for Runs 1103, 1104 and 1202, are not well explained by the relationship between the off-gas dew point and the temperature of the inlet coolant to the disproportionator condenser. Run 1104 had no calculated losses despite having a calculated sum of B₂H₆ and HCl partial pressures higher than B₂H₆ vapor pressure curve, whereas Runs 1103 and 1202 had appreciable calculated losses which were not explainable by presumed

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condensation of B_2H_6 and HCl on the condenser. The losses in Runs 1103, as in Run 1102 for which a complete material balance was not available, may be due to back reaction in absorber liquid phase at about $120^\circ F.$, as previously discussed. The inability to correlate the material balances for Runs 1104 and 1202 with $(B_2H_6 + HCl)$ dew point may be due to unknown discrepancies in measurements. It is significant that no such difficulty was encountered for the eight runs in the group, Run 1301 through 1401B, all of which were made under the best controlled conditions.

The surge in disproportionator gas rate and the high percentage of B_2H_6 in the off-gas which were noted during Run 1302 offer quantitative evidence of the deposition of liquid B_2H_6 plus HCl on the condenser surface. Calculations from data in Table 46 show that at steady state, about 3.5×10^{-4} lb. moles B_2H_6 would condense per hour. About 0.05×10^{-4} lb. moles HCl would also condense if these two components were condensed in proportion to their ratio in the off-gas. Since the disproportionator had been operating at steady state for at least one hour, it is clear that at least 3.5×10^{-4} lb. moles of B_2H_6 were condensed and available to furnish the minimum of 2.4×10^{-4} lb. moles of "extra" gas which flowed during the 75 second period following the stoppage of coolant supply. Further, it is easy to see how the B_2H_6 pocket caused by sudden volatilization of B_2H_6 into the slowly moving gas stream of the condenser section could maintain a high concentration such as 94.7 per cent B_2H_6 , which was obtained for an off-gas sample taken at the conclusion of the run.

PILOT PLANT DESIGN

I. Background Information

The design of the pilot plant was begun during the late stages of the laboratory and prepilot plant investigations and, of course, was based on information developed in this coordinated program. While the incomplete status of these investigations presented some handicap to the design engineers, there was also an advantage in that the still active program could be directed toward providing data deemed most critical.

The site selected for the pilot plant was American Potash & Chemical Corporation's Henderson, Nevada facility where previous prepilot plant work, as described in Section I of this report, had been carried out. This location offered the advantages of available space, an adequate supply of utilities, a dry, warm climate for an outdoor plant, a well-equipped laboratory, proximity to prepilot plant equipment to supplement the pilot plant, and an operating team experienced in handling borane.

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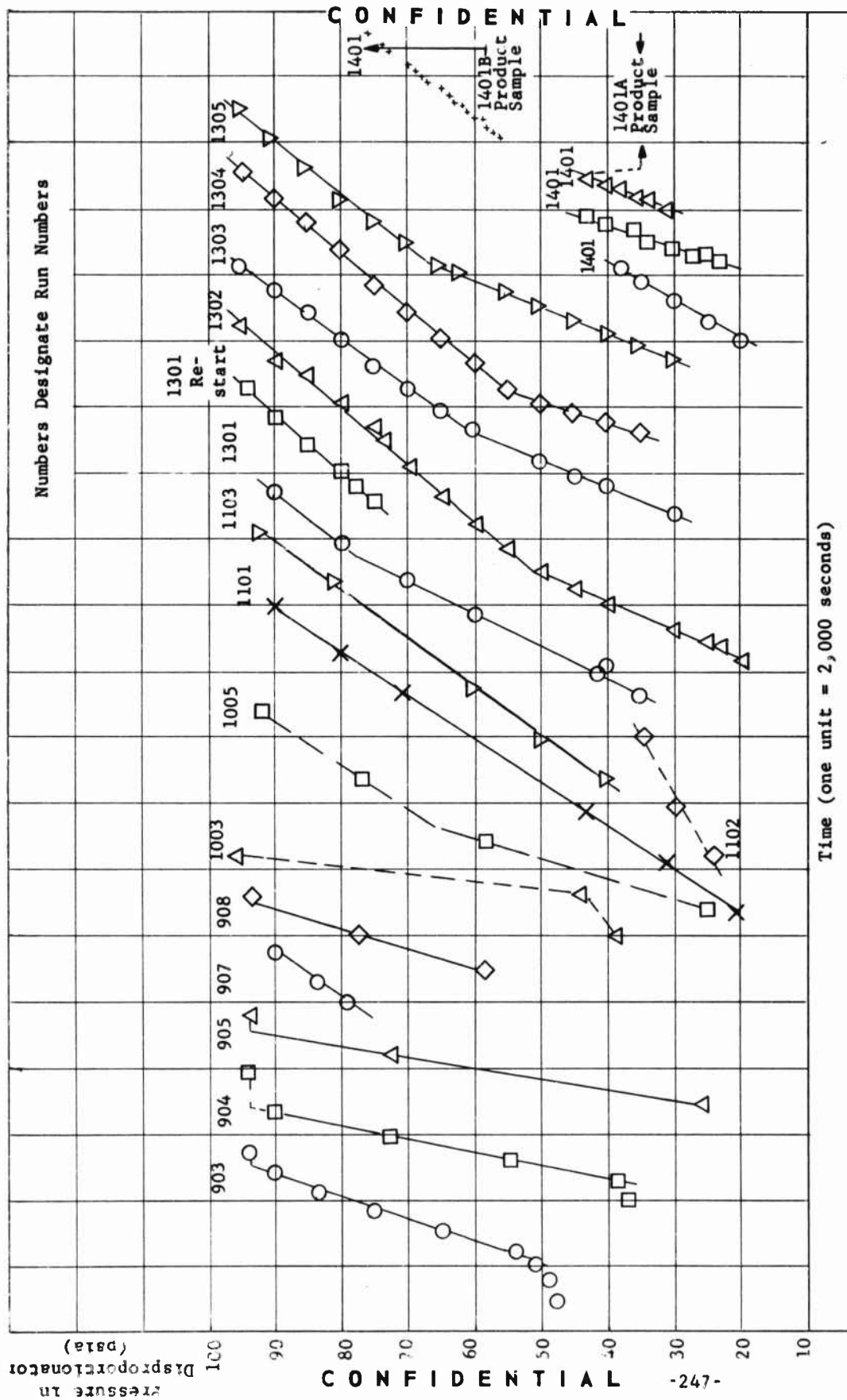


Figure 38. Build-Up of Pressure in Disproportionator Before Opening Back Pressure Control Valve

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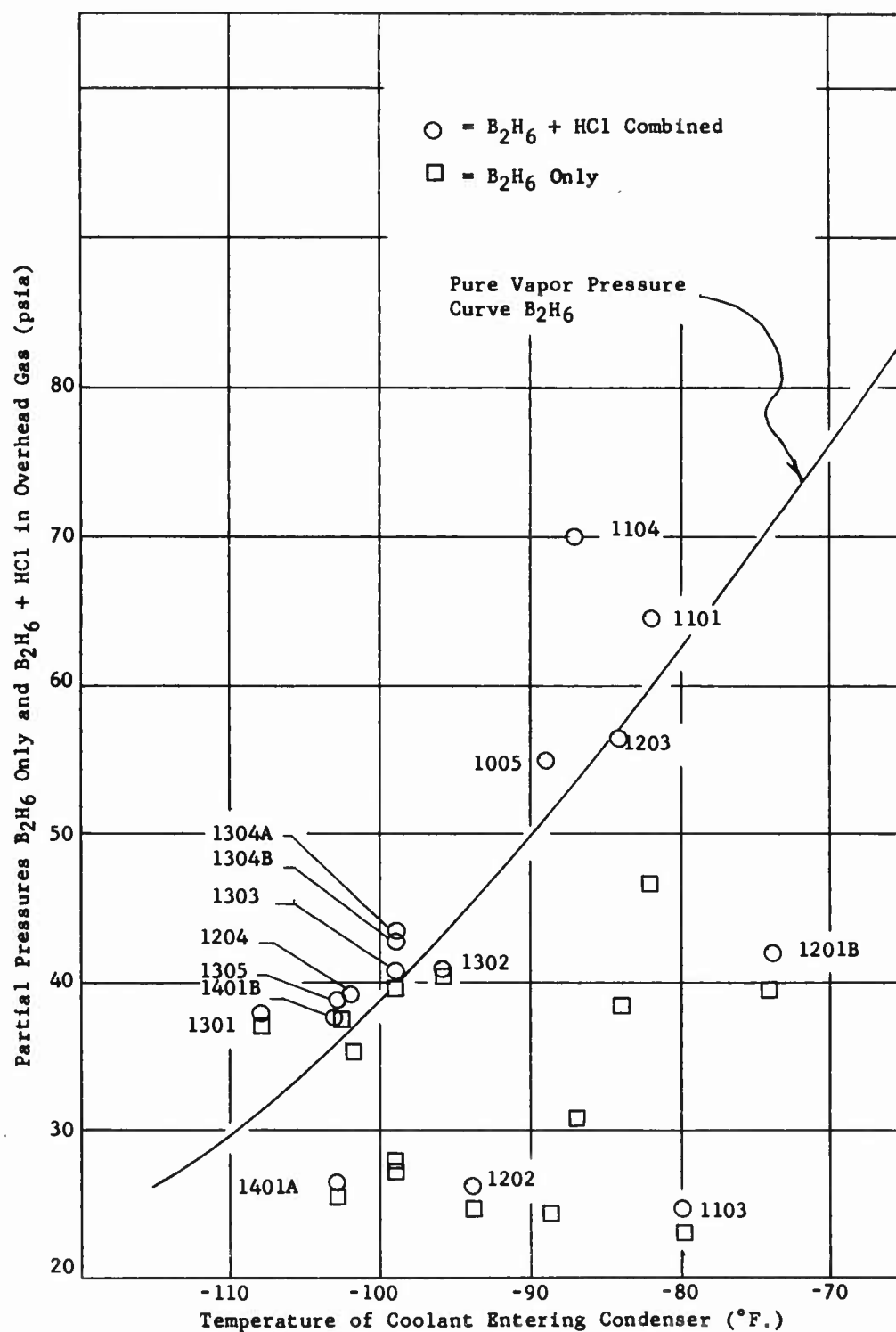


Figure 39. Partial Pressures B_2H_6 and HCl in Overhead Gas vs. Disproportionator Coolant Temperature

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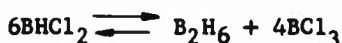
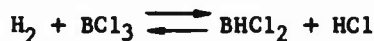
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Detailed design and engineering was initiated 1 December 1959 upon receipt of a letter contract from the Air Force. An abbreviated engineering and construction schedule was necessary with equipment procurement and installation proceeding as rapidly as engineering details were decided upon. Field construction was started 29 February 1960; the first lines were accepted by AFN representatives in early June; and final acceptance of the B₂H₆ plant occurred on 19 August 1960. Views of the finished pilot plant, which include the pyrolysis unit as well as the diborane unit, are presented in Figures 40 through 43.

The Bechtel Corporation of San Francisco, California carried out the detailed design and construction activities under subcontract to AFN, Inc. Engineering and construction surveillance was provided by American Potash & Chemical Corporation personnel.

II. Design Criteria

The two chemical reactions studied in the laboratory and prepilot plant formed the basis for the diborane process:



A. Product

Both diborane and hydrogen chloride were to be recovered in a pure state (99+%).

B. Plant Capacity and Yield

The operating requirement of the plant was a nominal 50 pounds per day of pyrolysis product. To accomplish this in view of uncompleted laboratory experimental work, the most optimistic yields were used and the design capacity was doubled to 100 pounds per day. This, it was felt, would compensate for lowered yields and still provide 50 pounds per day operating capacity requirement. The design capacities of the various units are listed below. Included is the boron trichloride feed preparation plant which was used to purify by redistillation available boron trichloride.

Boron Trichloride Feed Preparation Plant

		<u>lbs./hr.</u>	<u>lbs./day</u>
Capacity	BCl ₃	600	2500 (Batch)
<u>Diborane Plant</u>			
Feed	BCl ₃	63.7	1529
	H ₂	3.3	79
Product	B ₂ H ₆	7.5	180
	HCl	59.4	1426

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These quantities reflect complete conversion of feed materials to B_2H_6 and HCl , i.e., 100 per cent yield. This optimistic approach was justified inasmuch as no detectable quantities of side products had been produced in laboratory and prepilot plant experiments under optimum conditions. Obviously no allowance was made for physical losses.

C. Raw Materials

1. Boron Trichloride

Prepilot plant investigations had indicated that a high purity BCl_3 was necessary to insure a long life for the hydrogenation catalyst and to avoid reactor plugging. Therefore, the following specifications were established:

Boron Trichloride	- 99.7 wt. % (minimum)
Phosgene	- 0.10 mole % (maximum)
Free Chlorine	- 0.10 mole % (maximum)
Silicon as Si	- 300 ppm (maximum)
Sulfur Dioxide	- None
Carbon Tetrachloride	- None

Material meeting these specifications was commercially available and purchased with a certified analysis required of the supplier. In addition, the Air Force made available a considerable quantity of a lower grade BCl_3 containing approximately 0.30 mole per cent phosgene. A feed preparation plant was therefore designed to produce specification grade material from this BCl_3 by means of a distillation operation.

2. Hydrogen

Hydrogen as regularly produced by commercial suppliers was considered satisfactory. Specifications were:

Hydrogen	- 99.9% (minimum)
Oxygen	- 5 ppm (maximum)
Dew Point	- $-97^{\circ}F.$ (maximum)

Again, a certified analysis was required of the supplier.

3. Nitrogen

Nitrogen was required for use in purging and inerting of process equipment. Prepilot plant experience proved the regular industrial grade liquid nitrogen, having a guaranteed minimum purity of 99.997 per cent, to be very adequate. Its use was continued in the pilot plant.

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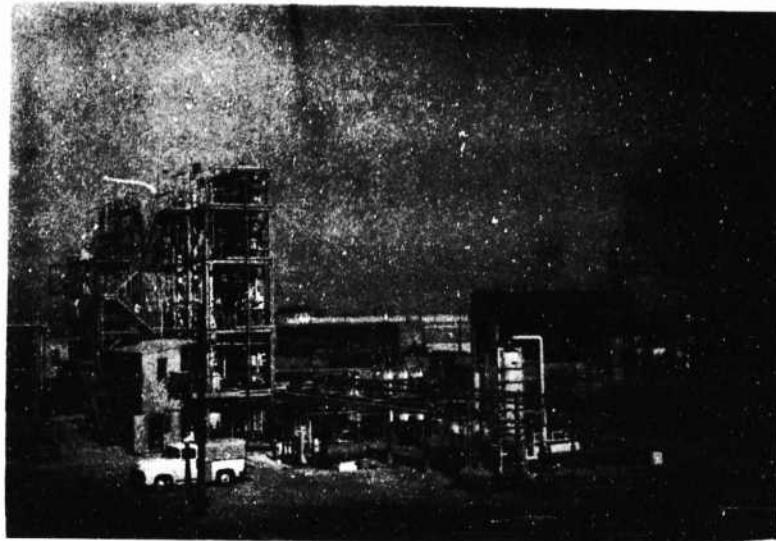


FIGURE 40. AFN PILOT PLANT
HENDERSON, NEVADA



FIGURE 41. AFN PILOT PLANT
DIBORANE PLANT - LEFT
PYROLYSIS PLANT - RIGHT

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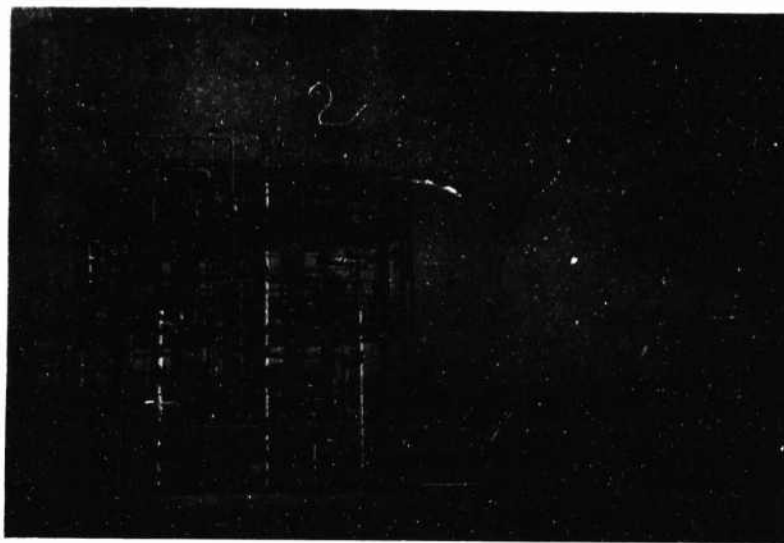


FIGURE 42. DIBORANE PILOT PLANT
SOUTH ELEVATION



FIGURE 43. DIBORANE PILOT PLANT
EAST ELEVATION
HYDROGENATION REACTOR IN FOREGROUND

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D. Hydrogenation Reactor

Operating conditions for this critical processing step were selected as follows:

H ₂ /BCl ₃ in Feed (mole ratio)	- 3
Reactor Temperature (°F.)	- 1292
Reactor Pressure (psig)	- 185
Residence Time (seconds)	- 0.2
Per Pass Conversion of BCl ₃ (%)	- 20

E. General Considerations

1. Storage

Provisions were made for the storage of both diborane and anhydrous hydrogen chloride as liquids. Refrigeration to approximately -20°F. was therefore required to limit pressure in the storage vessels to a nominal 200 psig.

Total storage capacity for 500 pounds of B₂H₆ was provided in two tanks. This amount was sufficient to feed the pyrolysis plant for at least five days and thus simultaneous operation of the diborane and pyrolysis plants was unnecessary.

Since no reuse of the hydrogen chloride by-product was intended, only 1500 pounds of storage capacity in a single tank, coupled with facilities for periodic sewerage, was necessary.

Three 220-gallon tanks provided a total storage capacity of 7000 pounds of purified BCl₃. Intermittent operation of the feed preparation step was therefore adequate to supply the requirements for the B₂H₆ plant.

Hydrogen was supplied from vendor furnished trailers containing a nominal 60,000 standard cubic feet. In addition, a bank of 120 stationary cylinders held a reserve of 50,000 standard cubic feet.

2. Sparing of Mechanical Equipment

No mechanical equipment was duplicated because the additional capital expense required was not justified by the purpose of the plant.

3. Type of Construction

"Outdoor" construction was utilized to the fullest extent possible with only nominal instrument and personnel protection. This arrangement was consistent with best safety practices and required minimum capital investment.

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4. Safety

The materials involved in diborane production presented a sobering array of safety hazards requiring careful engineering consideration:

Flammable Gases	- Hydrogen, dichloroborane, diborane, natural gas
Pyrophoric	- Dichloroborane, diborane
Toxic	- Boron trichloride, dichloroborane, diborane, hydrogen chloride
Corrosive	- Boron trichloride, dichloroborane, hydrogen chloride, sodium hydroxide (in destructive scrubber)

Certain criteria were therefore developed for the design and operation of the pilot plant:

- a. A positive pressure was maintained at all times to prevent entrance of air or water vapor into the equipment. Any leakage, therefore, must be outward.
- b. The only way in which an explosion can occur inside the equipment is if air has been admitted. If condition (a) is always maintained, an internal explosion cannot occur.
- c. Outdoor construction greatly reduced the hazards of exposure to personnel of toxic gases and pockets of flammable materials. Toxic concentrations or large concentrations of pyrophoric or flammable compounds were thus reduced to a minimum.
- d. The system was basically leaktight. It was thoroughly pressure tested at 100 psig pressure or above before being accepted from the contractor.
- e. Normal process pressures ranged from a low of 10 lbs./sq.in. to a high of 300 lbs./sq.in. Any excessive pressure would be relieved through a destruction scrubber to the atmosphere. All vessels containing potentially explosive materials were protected with two parallel rupture discs and one safety relief valve. One rupture disc was backed up with the relief valve, and set to relieve at a pressure approximately 30% lower than the vessel design rating. The parallel rupture disc was set for a pressure slightly less than the vessel design rating.

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All other vessels were furnished with a bursting disc and the back-up relief valve. All vessels were constructed to meet A.S.M.E. code specifications and were tested to withstand pressures of one and a half times design rating.

- f. Special alloys were specified for vessels used at temperatures at -50°F. or below. This precaution was intended to avoid embrittlement and possible fracture of the metal if the equipment were exposed to a sudden sharp impact. The lowest temperature in the plant was -100°F.

Special stainless steel and nickel alloys were used for the Step I furnace-reactor operating at 1300°F. and 185 lbs./sq.in. pressure. Normal carbon steel construction was used throughout the balance of the plant where temperatures ranged from minus 20°F. to plus 275°F.

- g. The destruction scrubber and all of the header lines to it (into which the vessel blowdowns empty) were maintained under a constant purge of natural gas to prevent entrance of air and moisture. The natural gas purge prevented the reaction of any of the system components with oxygen or water. All of the gases then passed through a caustic soda solution in the destructive scrubber tower before being vented to the atmosphere.

A 10-inch water seal was maintained on the top tray of the scrubbing tower. This seal held a positive natural gas pressure in the blowdown system and prevented any backflow of air into the destruction scrubber and the blowdown lines both during normal operations and in case of a major relieving. If the water seal were lost, a 2-inch gas line at 35 lbs./sq.in. pressure automatically discharged into the destruction scrubber to prevent any entry of air back into the system.

- h. The diborane and pentaborane storage vessels were mounted behind concrete block walls.
- i. During normal operations, the operating personnel spent a large percentage of their time at the control panel. The control area was directly protected from the equipment by a solid floor and roof, sheet-metal wall to the rear, and an observation partition with Lucite windows on the process side of the structure. This semienclosure provided a means of protecting the operators from direct exposure to a sudden release of liquids or gases resulting from an equipment leak, and gave them time either to put on an air mask or to leave the area.
- j. At every level of the operating structures and throughout the area at grade level, air hoses were mounted for immediate connection to air masks. Each operator was furnished with an air mask for his immediate use.

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- k. Two avenues of escape were provided at every level of the structures: (1) an external stairway route, and (2) a fireman's type escape pole for emergency use.
- l. The pilot plant was a restricted area and only authorized personnel could enter. No smoking or open fires were permitted in the area, and explosion-proof motors and push-button stations were used throughout the plant. The switchgear in the electrical control room was of non-explosion proof construction; however, a constant stream of fresh air was forced into the room by a blower to prevent the build-up of flammable concentrations of gases in case of a leak or spill.
- m. Fire extinguishers were located at all levels of the structure and at grade level. In addition, several large water hose stations were located nearby. It must be noted, however, that there is no absolutely proven fire extinguishing agent for boron hydride fires. The best fire procedures involve (1) shutting off the source of the burning materials by closing valves, etc., and (2) isolating and keeping the intensity of the fire down to protect adjoining areas with available fire fighting equipment.
- n. To aid in preventing the danger of fires or explosions in one area spreading to another location, the diborane unit was erected approximately 50 feet from the pyrolysis unit. Within the diborane area, the furnace was 50 feet from the main structure, and the hydrogen cylinder storage area another 50 feet away. The destruction scrubber was also 50 feet from the Step I structure. Isolating the scrubber from the processing area minimized the possibility of noxious vapors that might pass through the scrubber floating back into the operating areas.

The production of diborane, in view of the nature of the chemicals involved, can never be considered anything but a hazardous operation. Nevertheless, the safeguards outlined, when coupled with diligent safety performance on the part of operating and maintenance personnel, provided a high degree of security consistent with the purpose of the plant and the funds available.

5. General Design Specifications

As a means of assuring quality of materials and construction, nationally recognized codes and standards were utilized in the design of equipment and in the specifications for materials, equipment, and services purchased. In addition, inspections were performed in the vendors' shops during fabrication and in the field during construction to insure conformance to those requirements and to other purchase specifications.

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The codes and standards utilized included the following:

ASME Unfired Pressure Vessel Code, Section VIII,
latest revision

ASA Code for pressure piping, latest revision

TEMA (Tubular Exchanger Manufacturers Association) standards

National Electric Code

NEMA (National Electrical Manufacturer's Association) standards

ASTM (American Society for Testing Materials) standards

Underwriters Laboratories standards

American Concrete Institute's code for reinforced concrete

American Institute of Steel Construction specification

Applicable state and local codes

III. Process Description

A. Diborane Production (Step I)

Two flowsheets are presented for the diborane plant. Figure 44 is a simplified version which facilitates the understanding of the general plant operation. Figure 45 presents in more detail the sizing of equipment, actual flow patterns, and the operating conditions. Supplementing these is the design material balance given in Table 53. Still more detail is presented in Appendix I which includes piping and instrument diagrams and a plot plan. The diborane production unit is referred to as Step I of the pilot plant.

The hydrogenation of boron trichloride was accomplished in a gas-fired, silver lined furnace-reactor (1F-1,2). The reactor effluent gases were rapidly quenched in an exchanger (1E-1), also silver lined, to "freeze" the favorable high temperature equilibrium. The reactor products were then contacted with cool boron trichloride in the primary absorber (1C-1) to separate hydrogen and hydrogen chloride as an overhead stream from dichloroborane and boron trichloride as a bottom stream. Hydrogen stripping gas introduced into the bottom of the primary absorber stripped hydrogen chloride out of the bottom stream and into the overhead stream.

The primary absorber overhead was chilled and sent to the secondary absorber (1C-2) where it was contacted with chilled boron trichloride to

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absorb the HCl. The overhead of this column (H_2) was recycled, and the bottoms (HCl and BCl_3) were sent to the HCl fractionator (1C-5).

Liquid anhydrous HCl was produced as the overhead product of the fractionator, and sent to Tank 1C-9 for storage. Periodically this by-product, HCl, was hydrolyzed and sewerred. The bottoms product of the HCl fractionator, essentially pure BCl_3 , was recycled. A small amount of H_2 , dissolved in the feed to the column, was separated from the fractionator overhead product as a gas, and recycled to the secondary absorber.

The primary absorber (1C-1) bottoms product contained dichloroborane and BCl_3 . This material was sent to the prefractionator (1C-3). Recycle BCl_3 was separated as a bottoms product, and the dichloroborane disproportionated to form B_2H_6 gas, and the B_2H_6 , saturated with dichloroborane and BCl_3 , was sent to the disproportionation tower (1C-4). Disproportionation of the dichloroborane was completed in this tower, and liquid B_2H_6 obtained as the overhead product by fractionation. The B_2H_6 was sent to storage (1C-7A, -7B) for use later as feed to the pyrolysis plant (Step II). Since the tower bottoms product contained some dichloroborane, it was recycled to the prefractionator.

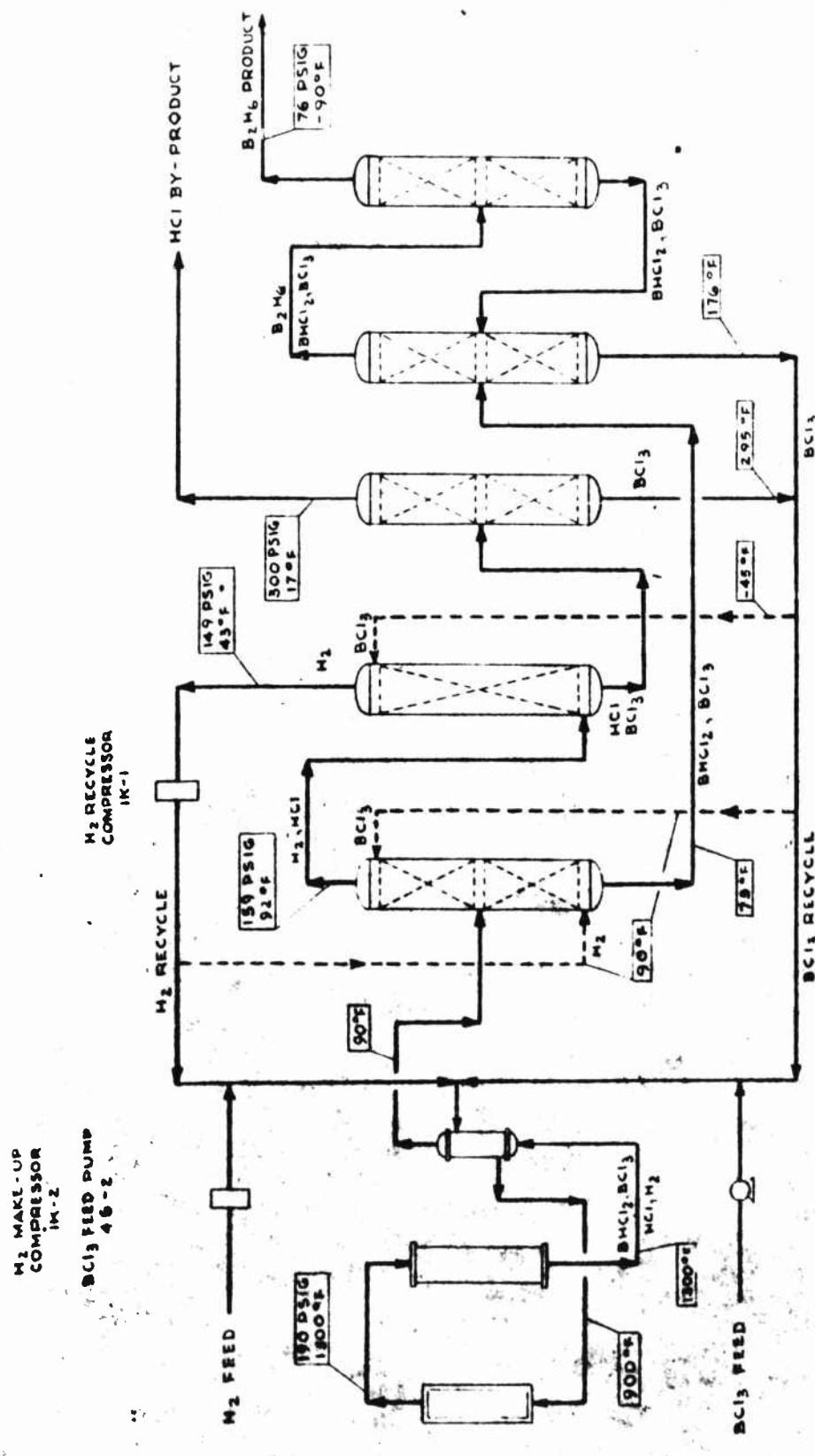
B. Feed Preparation (Step IV)

Boron trichloride not meeting 0.10 per cent maximum phosgene content and/or containing high boiling impurities was fractionated in the feed preparation section. The purified feed was stored for subsequent pumping to the diborane plant where it was used as feed and absorbent. Figure 46 describes the equipment and gives material and energy balances on the distillation equipment and storage tanks. A hydrogen fixed storage and a mobile refill unit, both furnished by the vendor, are indicated in this drawing. No processing of the hydrogen prior to use was required.

C. Refrigeration Plant (Step V)

A unique three-stage refrigeration system using refrigerant R-22 was designed to provide three levels of refrigeration at $-20^\circ F.$, $-50^\circ F.$, and $-100^\circ F.$ Figure 47 is a simplified flowsheet of the refrigeration system. Liquid refrigerant was pumped from a chilled supply tank (5C-2) to the $-20^\circ F.$ and $-50^\circ F.$ loads. Refrigerant returning from the $-20^\circ F.$ loads passed to the $-20^\circ F.$ accumulator from which the vaporized refrigerant was compressed (compressor 5K-3) and distributed back to the supply tank after being chilled in the $-50^\circ F.$ accumulator. Liquid from the $-20^\circ F.$ accumulator also returned to the pump tank (5C-2). The vaporized refrigerant returning from the $-50^\circ F.$ loads returned to the $-50^\circ F.$ accumulator. From there it was compressed (compressor 5K-2) and passed to the $-20^\circ F.$ accumulator for cooling. Liquid in the $-50^\circ F.$ accumulator was vaporized to provide cooling for liquid passing through the accumulator to the pump tank and to the $-100^\circ F.$ load. Vapor from the $-100^\circ F.$ load was compressed (compressor 5K-1) and cooled in the $-20^\circ F.$ accumulator.

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FURNACE REACTOR IF-1
 REACTOR FEED EFFLUENT EXCHANGER IE-1
 PRIMARY ABSORBER IC-1
 SECONDARY ABSORBER IC-2
 HCl FRACTIONATOR IC-5
 PRIMARY DISPROPORTIONATOR COLUMN IC-3
 SECONDARY DISPROPORTIONATOR COLUMN IC-4

FIGURE 44

AFN, Inc.
LOS ANGELES, CALIFORNIA

DATE 4-4-60	DRAWN N. REGAN	AFN PILOT PLANT DIAGRAM OF STEP 1 PROCESS FLOWSHEET	DRAWING NO.
SCALE —	APPROVED		PFS-263

NOTE: ABSORBER IC-2
NOT ILLUSTRATED
IN THIS DIAGRAM

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1E-1 & 1P-2

COMBINED FEED HEATER
& REACTOR

DUTY: 90.4 MBTU/HR (TO PREHEAT)
40.8 MBTU/HR (TO REACTOR)

1E-1

REACTOR FEED
EFFLUENT EXCH'G

DUTY: 226.0 MBTU/HR (MAX)
100.7 MBTU/HR (MAX)

1E-2

BCL VAPORIZER

DUTY: 7.9 MBTU/HR

1E-6

REACTOR EFFLUENT
COOLER

DUTY: 226 MBTU/HR

1E-6

RECYCLE HYDROGEN
COOLER

DUTY: 6.5 MBTU/HR (MAX)
7.7 MBTU/HR (MAX)

1C-1

PRIMARY
ABSORBER

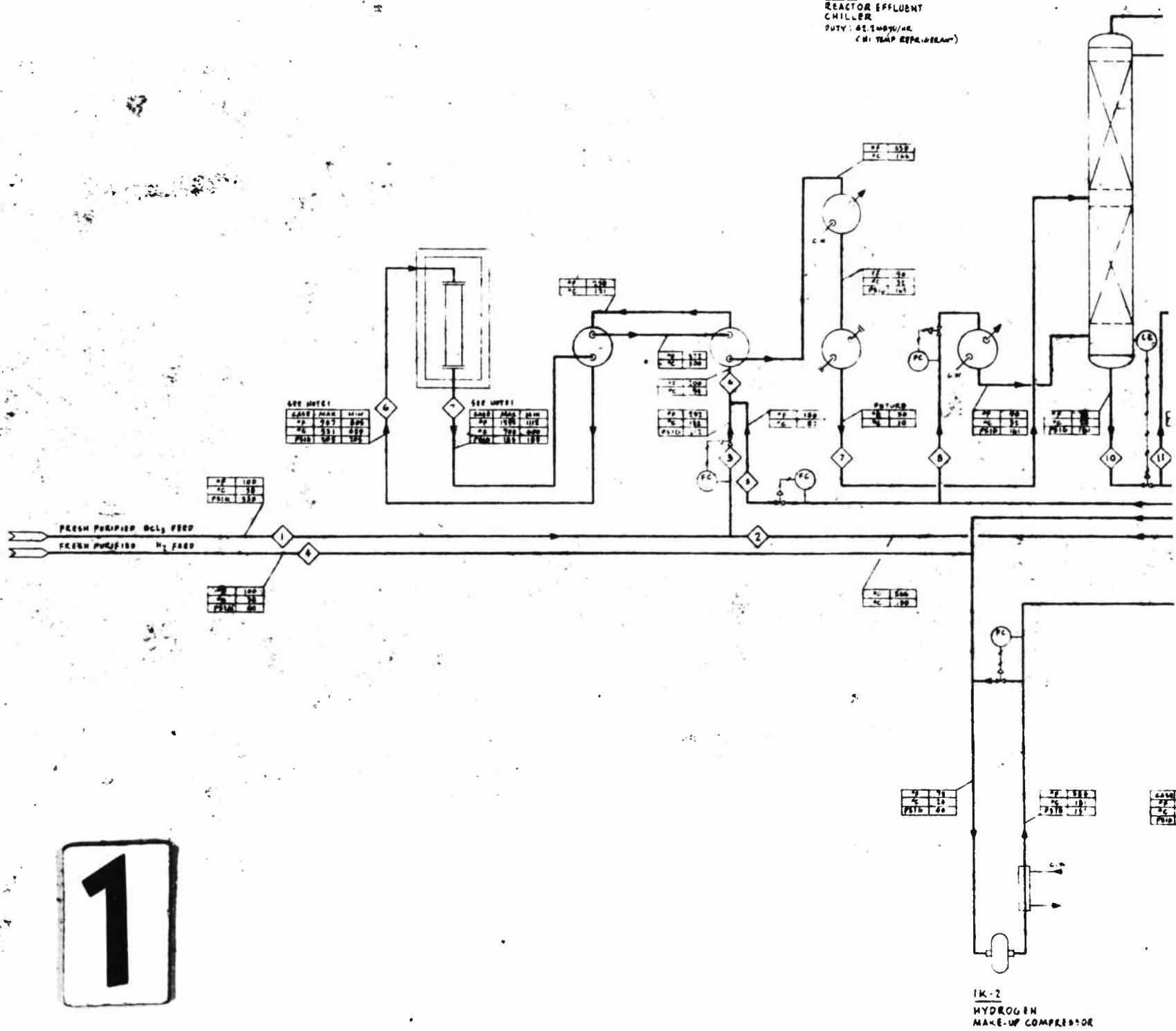
10' x 55' x 2

(FUTURE)

1E-7

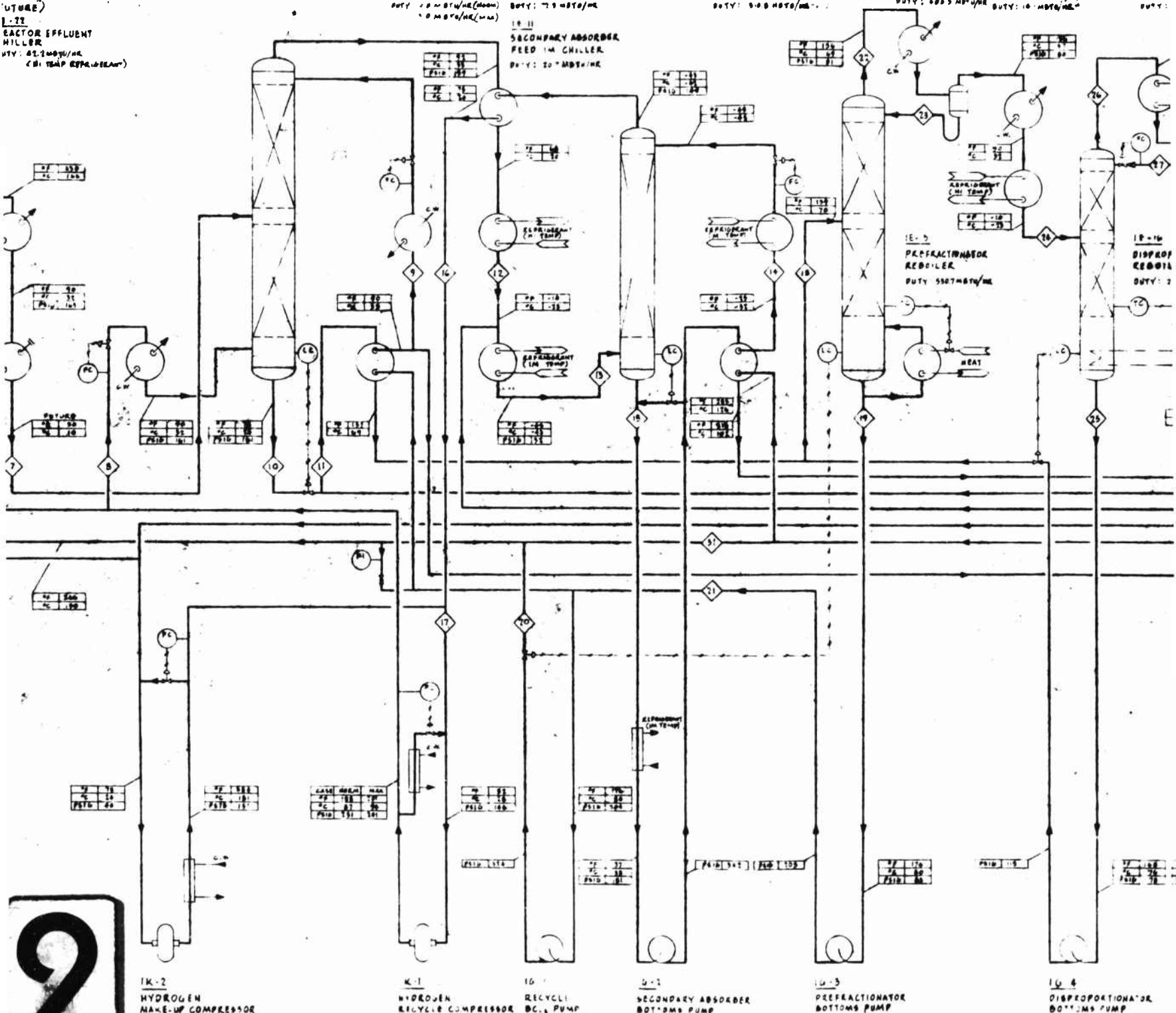
REACTOR EFFLUENT
CHILLER

DUTY: 62.2 MBTU/HR
(W/ TRAP REPAIR/REPAIR)

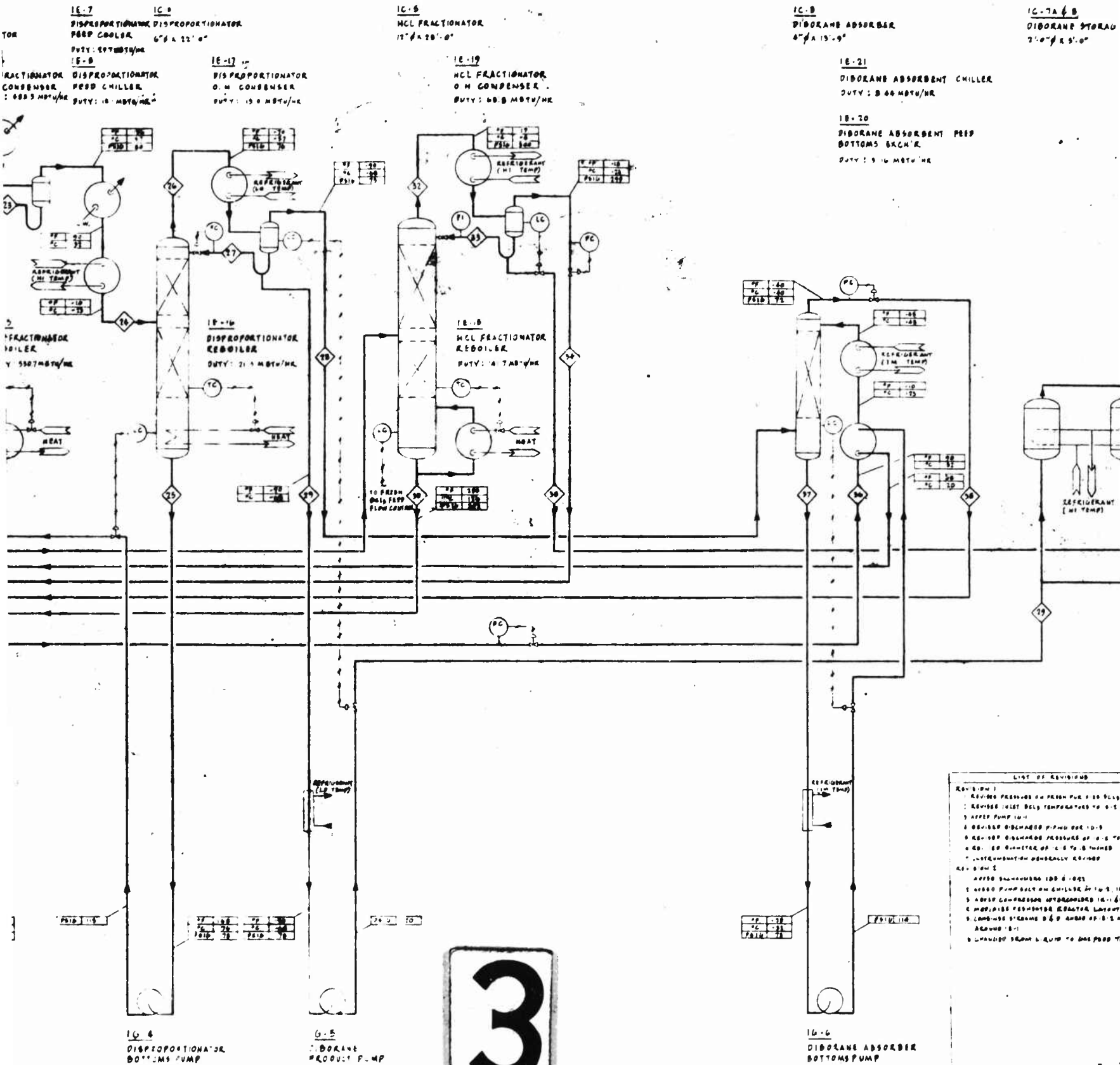


E-6 REACTOR EFFLUENT COOLER
 DUTY: 92.6 MBTU/HR
 1E-6 RECYCLE HYDROGEN COOLER
 DUTY: 6.5 MBTU/HR (NORM)
 7.7 MBTU/HR (MAX)
 1C-1 PRIMARY ABSORBER
 10'0" x 95'0"
 1E-8 REFRACT. FEED PRIMARY ABSORBENT EXCH'G
 DUTY: 28.9 MBTU/HR
 E-7 PRIMARY ABSORBENT FEED COOL'G
 DUTY: 2.8 MBTU/HR (NORM)
 3.0 MBTU/HR (MAX)
 E-9 SECONDARY ABSORBER FEED CHILLER
 DUTY: 7.5 MBTU/HR
 1C-2 SECONDARY ABSORBER
 6'0" x 23'0"
 1E-10 SECONDARY ABSORBENT FEED CHILLER
 DUTY: 7.5 MBTU/HR
 1E-11 SECONDARY ABSORBENT FEED IM CHILLER
 DUTY: 20.7 MBTU/HR
 1E-12 SECONDARY ABSORBENT ALL FRACTIONATOR FEED EXCH'G
 DUTY: 5.0 MBTU/HR
 1C-3 DCB FRACTIONATOR
 10'0" x 84'0"
 1E-14 FRACTIONATOR 0 M. CONDENSER
 DUTY: 60.5 MBTU/HR
 1E-7 DISPROPORTIONATOR DISPROPORTIONATOR FEED COOLER
 6'0" x 22'0"
 DUTY: 69.7 MBTU/HR
 1E-8 DISPROPORTIONATOR FEED CHILLER
 DUTY: 10.4 MBTU/HR
 1C-4 DISPROPORTIONATOR
 6'0" x 22'0"
 1E-17 DISPROPORTIONATOR
 DUTY: 10.4 MBTU/HR

1E-22 REACTOR EFFLUENT MILLER
 DUTY: 82.2 MBTU/HR
 (BI TEMP APPROXIMATE)



2



- LIST OF REVISIONS
- REVISION 1
1. REVISED PRESSURE ON FEED PUMP TO 20 PSIG
2. REVISED FEED DCL TEMPERATURE TO 0.5 °F
3. ADDED PUMP 10-1
4. REVISED DIBORANE PUMP SET TO 0.5
5. REVISED DIBORANE PRESSURE OF 0.5 TO 1
6. REVISED DIAMETER OF 1C-8 TO 8 INCHES
7. INSTRUMENTATION GENERALLY REVISED
- REVISION 2
1. ADDED SHUT-OFF VALVE TO 1C-5
2. ADDED PUMP SET ON CHILLER TO 10.5 PSIG
3. ADDED COMPRESSOR AUTOREGULATED TO 1.6 MP
4. MODIFIED FEED-BOTTOMS EXCHANGER LAYOUT
5. COMPRESSOR SYSTEMS D & B ADDED TO 1C-5 AND
ADDED TO 1C-6
6. CHANGED STREAM 6 ROUTE TO ONE PASS TO

1C-8
HCL FRACTIONATOR
12" DIA 10'-0"

1E-19
HCL FRACTIONATOR
O M CONDENSER
DUTY: 600 MBTU/HR

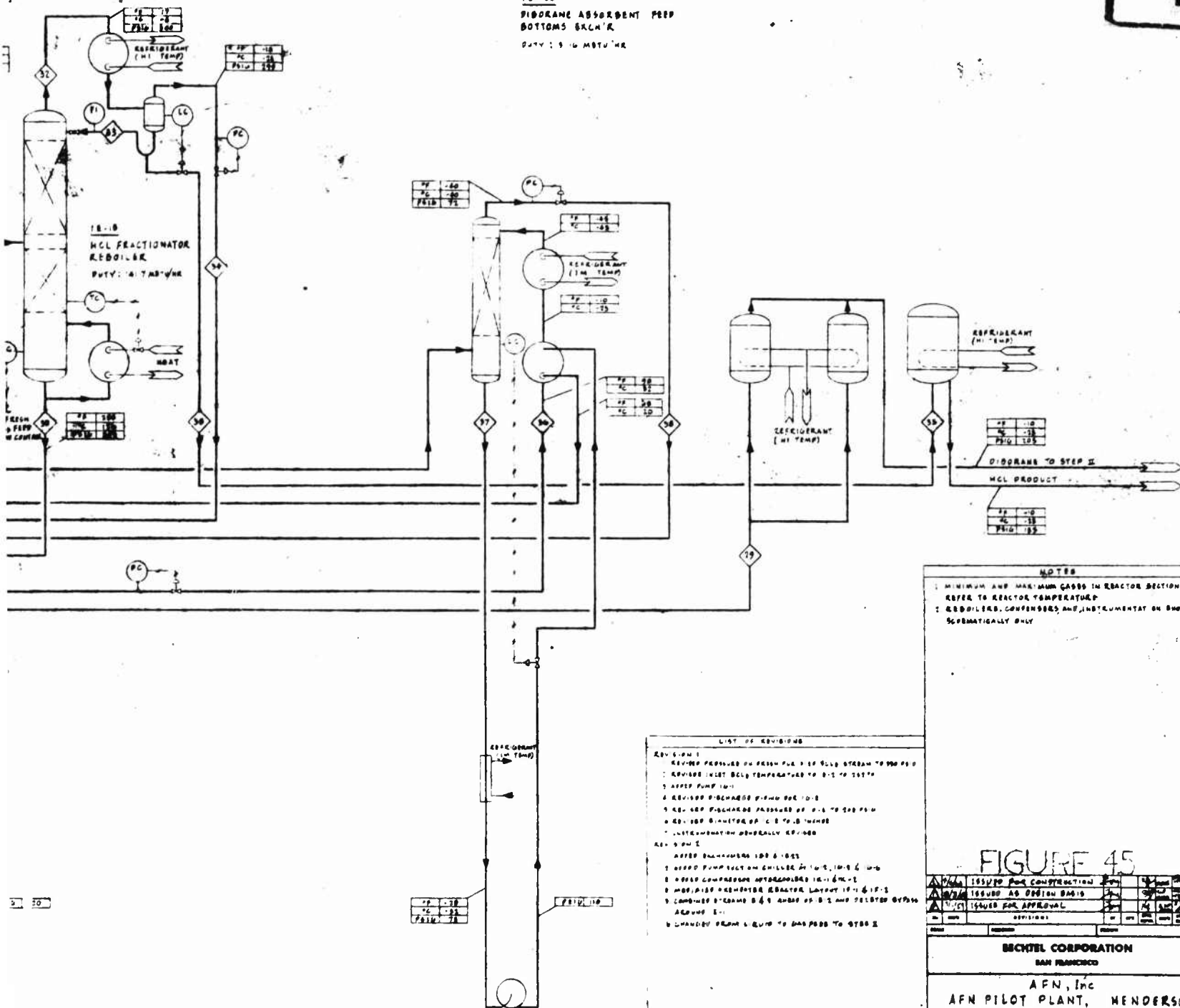
1C-8
DIBORANE ABSORBER
4" DIA 15'-9"

1E-21
DIBORANE ABSORBENT CHILLER
DUTY: 844 MBTU/HR

1C-7A & B
DIBORANE STORAGE
2'-0" DIA 4'-5'-0"

1C-9
HCL STORAGE
3'-0" DIA 9'-6"

4



- LIST OF REVISIONS
- REV 5-PM 1
 - REVISED PERMITS ON PUMP FOR 1 OF 500 PSIG
 - REVISED INLET BOLD TEMPERATURE TO 0-1 TO 100°F
 - ADDED PUMP 10-1
 - REVISED FLOWMETER PUMP FOR 10-1
 - REVISED FLOWMETER PASSAGE OF 0-1 TO 500 PSIG
 - REVISED DIMENSIONS OF 10-1 TO 10-2
 - REVISIONS GENERALLY REVISED
 - REV 5-PM 2
 - ADDED DIMENSIONS 10-1 & 10-2
 - ADDED PUMP 10-1 ON CHILLER 10-1 & 10-2
 - ADDED COMPRESSOR APPROPRIATE 10-1 & 10-2
 - ADDED DIMENSIONS REACTOR LAYOUT 10-1 & 10-2
 - COMBINED DIMENSIONS 10-1 & 10-2 AND RELATED BYPASS
 - REVISED 10-1
 - CHANGED FROM 10-1 TO 10-2 FOR STEP 2

NOTES

1. MINIMUM AND MAXIMUM GASES IN REACTOR SECTION REFER TO REACTOR TEMPERATURE
2. REBOILERS, CONDENSERS AND INSTRUMENTATION SHOWN SCHEMATICALLY ONLY

FIGURE 45

ISSUED FOR CONSTRUCTION	DATE	BY
ISSUED AS DESIGN BASIS	DATE	BY
ISSUED FOR APPROVAL	DATE	BY
REVISIONS		
NO.	DESCRIPTION	DATE
1	ISSUED FOR CONSTRUCTION	10/1/68
2	ISSUED AS DESIGN BASIS	10/1/68
3	ISSUED FOR APPROVAL	10/1/68
BECHTEL CORPORATION SAN FRANCISCO AFN, Inc. AFN PILOT PLANT, HENDERSON PROCESS FLOW DIAGRAM STEP 1 - CATALYTIC HYDROGENATION - LOW TEMPERATURE ABSORPTION PROCESS		
3192	I-RA-2	2

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TABLE 53
LOW TEMPERATURE ABSORPTION PROCESS MATERIAL BALANCE

STREAM NO.	1		2		3		4		5		6		7		8		9	
	FRESH BCl ₃ FEED		RECYCLE BCl ₃ FEED		TOTAL BCl ₃ TO REACTOR		FRESH H ₂ FEED		TOTAL H ₂ TO REACTOR		REACTOR CHARGE		REACTOR PRODUCTS		STRIPPING H ₂		ABSORB. TO PRIM. ABSORB.	
	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr
H ₂							1.63	3.3	24.45	49.3	24.45	49.3	22.82	46.0	10.0	20.2		
B ₂ H ₆																		
HCl													1.63	59.5				
DCB													1.63	134.9				
BCl ₃	0.54	63.7	7.61	891.4	8.15	955.1					8.15	955.1	6.52	764.0			25.0	2929.8
TOTAL	0.54	63.7	7.61	891.4	8.15	955.1	1.63	3.3	24.45	49.3	32.60	1004.4	32.60	1004.4	10.0	20.2	25.0	2929.8
Av. MW							2.02			2.02	30.81			30.81		2.02		

STREAM NO.	10		11		12		13		14		15		16		17		18	
STREAM	PRIM. ABSORB. BOTTOMS		LIQUID TO 1E-8		PRIM. ABSORB. OHD		TOTAL FEED TO SEC. ABSORB.		ABSORBENT TO SEC. ABSORB.		SEC. ABSORB. BOTTOMS		SEC. ABSORB. OVERHEAD (a)		TOTAL GAS TO H ₂ COMPRESSOR		TOTAL PREFRAC. TION WATER FEED	
	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr	mole/hr	lb/hr
H ₂	0.30	0.6	0.30	0.6	32.52	65.7	32.72	66.1			0.20	0.4	32.52	65.7	34.45	69.6	0.30	0.6
B ₂ H ₆			0.39	10.6													0.39	10.6
HCl					1.63	59.4	1.98	72.2			1.98	72.2						
DCB	1.63	134.9	1.63	134.9													1.81	149.9
BCl ₃	25.21	2954.3	28.21	3305.9	6.31	739.5	6.31	739.5	35.0	4102.0	41.31	4841.5					31.11	3645.5
TOTAL	27.14	2089.8	30.53	3452.0	40.46	864.6	41.01	877.8	35.0	4102.0	43.49	4914.1	32.52	65.7	34.45	69.6	33.61	3806.6
Av. MW						21.37		21.40						2.02		2.02		

(a) May contain 0.09 mole/hr BCl₃ stripped from absorber.

(continued)

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TABLE 53
(continued)
LOW TEMPERATURE ABSORPTION PROCESS MATERIAL BALANCE

STREAM NO.	19	20	21	22	23	24	25	26	27	28
STREAM	TOTAL PREFRAC- TIONATER BTMS	PREFRACT. BTMS. TO REACTOR	PREFRACT. TO 1C1 & 1C-8	PREFRACT. TOTAL OVHD	PREFRACT. REFLUX	DISPROP. FEED	DISPROP. BOTTOMS	DISPROP. TOTAL OVHD. VAPOR	DISPROP. REFLUX	DIBORANE ABS. FEED
	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr
H ₂				30 0.6		30 0.6		0.30 0.6		30 0.6
B ₂ H ₆				78 21.6	39 10.8	39 10.8		2.84 78.7	2.18 60.4	39 10.8
HCl										
DCB				18.89 1563.1	17.08 1413.2	1.81 149.9	0.18 15.0			
BCl ₃	29.30 3433.3	1.30 151.9	28.00 3281.4	40.24 4715.8	38.43 4503.6	1.81 212.2	2.90 339.6			
TOTAL	29.30 3433.3	1.30 151.9	28.00 3281.4	60.21 6301.1	55.90 5927.6	4.31 373.5	3.08 354.6	3.14 79.3	2.18 60.4	69 11.4
Av. MW				104.65				25.25		

STREAM NO.	29	30	31	32	33	34	35	36	37	38
STREAM	DIBORANE LIQ. PRODUCT	TOTAL HCl FRACT. BTMS	HCl FRACT. TO REACTOR	HCl FRACT. OVHD VAPOR	HCl FRACT. REFLUX	HCl FRACT. OVHD VAPOR PRODUCT	HCl LIQUID PRODUCT	ABS. TO DIBO- RANE ABSORBER	DIBORANE ABSORBER BOTTOMS	DIBORANE ABSORBER OVHD. VAPOR
	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr	mol/hr lb/hr
H ₂				0.20 0.4		0.20 0.4				0.3 0.6
B ₂ H ₆	27 7.5								0.39 10.6	
HCl				10.70 390.0	8.72 318.0	0.35 12.8	1.63 59.4			
DCB										
BCl ₃		41.31 4841.5	6.31 739.5					3.00 351.6	3.00 351.6	
TOTAL	27 7.5	41.31 4841.5	6.31 739.5	10.90 390.4	8.72 318.00	0.55 13.2	1.63 59.4	3.00 351.6	3.39 362.2	0.3 0.6
Av. MW				35.82		24.00				2.02

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BCl₃ SHIPPING
BOTTLE

4V-2
BCl₃ SCALE

4C-2
BCl₃ DISTILLATION COLUMN
8' x 12"
WT: 96

4E-2
BCl₃ DISTILLATION
OVHD. CONDENSER
PUT: 100 MBTU/HR

4C-4A, B & C
PURIFIED BCl₃
STORAGE TANKS
2.0 φ x 8-0

SIZED STORAGE UNIT
(BY OTHERS)

MOBILE ST
(BY OTHERS)

4E-3
BCl₃ COOLER
350 BTU/HR

TEMP	100
PSIG	10

BCl₃ DISTILLATION
OVHD. ACCUMULATOR
8' x 12"

COOLING WATER

TEMP	100
PSIG	10

4E-3
BCl₃ DISTILLATION
REBOILER
PUT: 300 MBTU/HR

40° STEAM

TEMP	100
PSIG	10

BOTTOMS TO
DECONTAMINATION

PHOSGENE OUT TO
DECONTAMINATION

CW

TEMP	100
PSIG	10

PSIG BAR

CYLINDER
(BY CLIENT)

4G-3
PURIFIED BCl₃ CHARGE PUMP

1

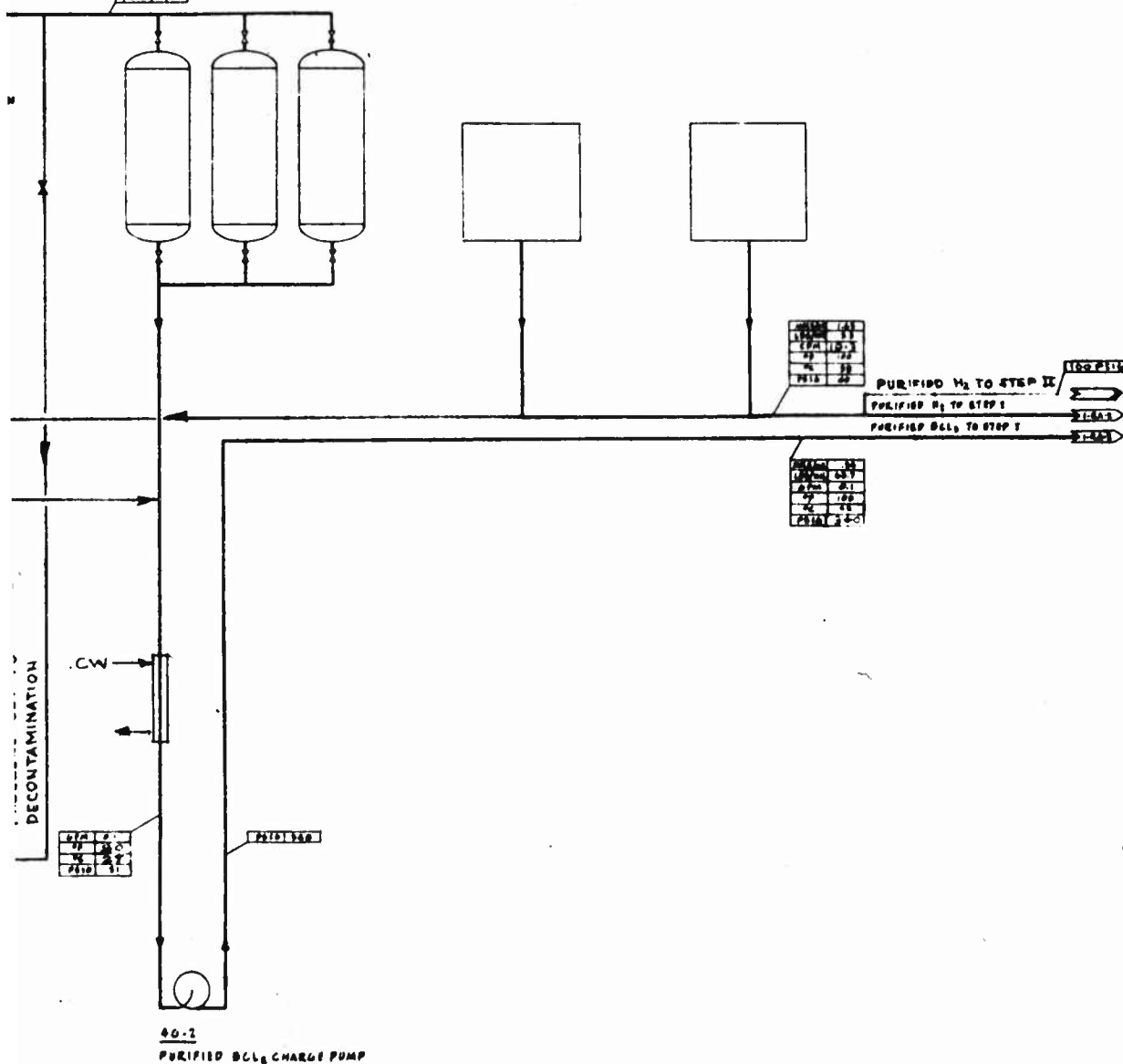
4C-6A, B & C
PURIFIED BCL₃
STORAGE TANKS
2.0 φ 8'-0

FIXED STORAGE UNIT
(BY OTHER)

MOBILE REFILL UNIT
(BY OTHER)

4E-3
BCL₃ COOLER
350 BTU/HR

ITEM	QTY
1	100
2	100
3	100



NOTE:
1. ALL PRESS. & TEMPERATURES LISTED REFER TO DESIGN VALUES.
2. COMPENSATE TO FLAME BACK TO ACCUMULATOR.

FIGURE 46

- LIST OF CHANGES FOR EDITIONS
- REV. 1
1. REVISED DISCHARGE PRESSURE 40-1 & 40-2
2. CHANGED H₂ FROM 100 PSI
3. REVISED 40-1, 40-2
4. REVISED PRESSURE ON BCL₃ TO STEP 1
- REV. 2
1. DELETED 40-1, 40-2, 40-3, 40-4, 40-5
2. ADDED CYCLING, FIXED STORAGE UNIT & MOBILE REFILL UNIT
3. REVISED 40-3 FROM ELECTRICAL HEATING TO STEAM
4. BCL₃ DIST. ON ACCUMULATOR CHANGED FROM EQUIPMENT TO PIPE
- REV. 3
1. REPLACED 40-2, 40-3 & 40-4 WITH LARGER SIZES
2. ADDED PHOSGENE TAKE-OFF LINE
3. ADDED COOLER TO 40-2 SUCTION
4. REVISED PIPING FROM BCL₃ CYLINDER

SHEET 5 OF 5

REVISED FOR NOTE ABOVE	DATE	BY	CHKD
ISSUED FOR APPROVAL	DATE	BY	CHKD
ISSUED FOR APPROVAL	DATE	BY	CHKD

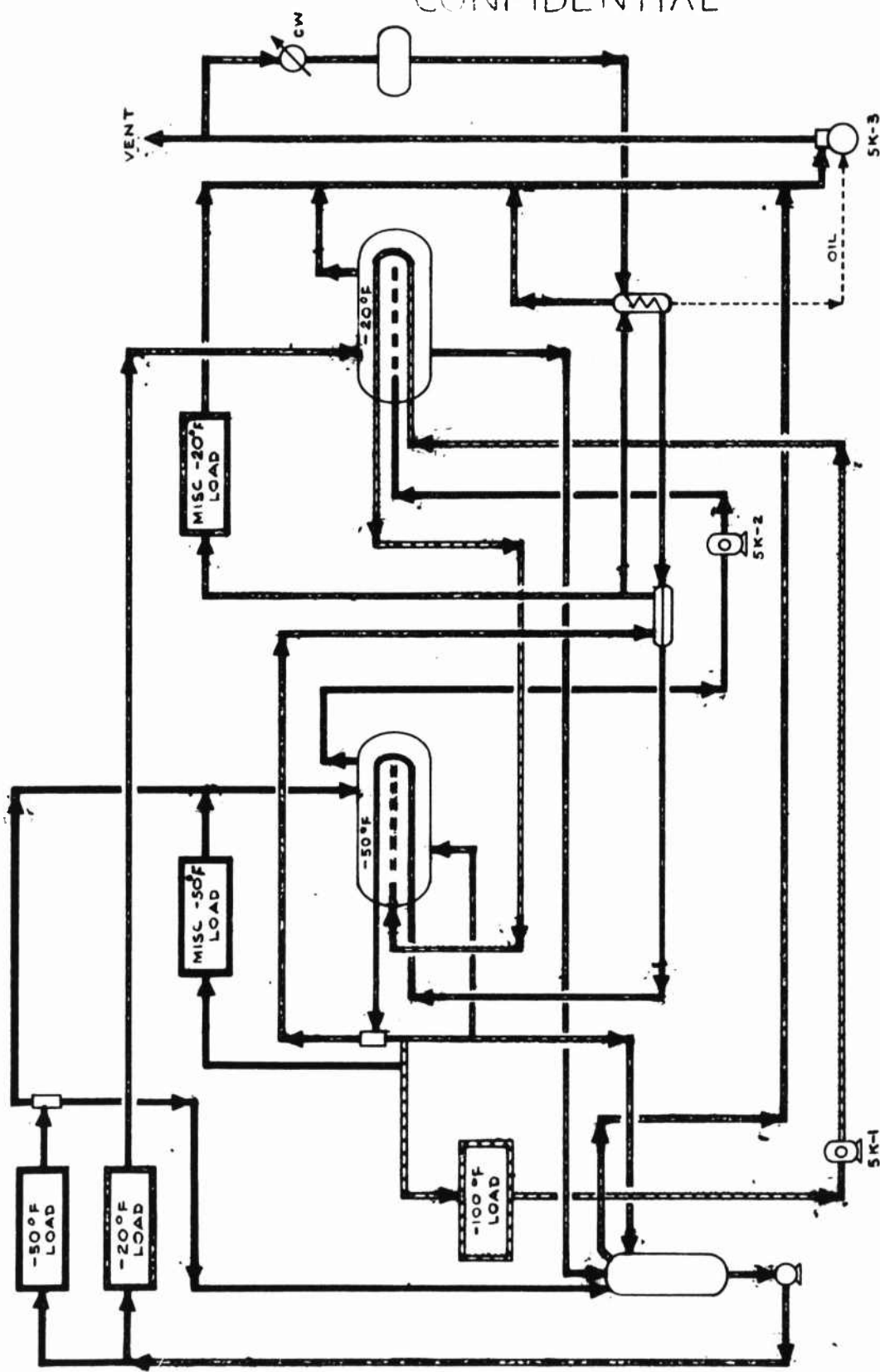
SCOTT CORPORATION
NEW HAVEN, CT

AFN, INC.
AFN PILOT PLANT, HENDERSON

PROCESS FLOW DIAGRAM
STEP 1 - CATALYTIC HYDROGENATION
FEED PREPARATION SECTION

3192	4-RA-1	3

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FIGURE 47

AFN, INC. LOS ANGELES, CALIFORNIA		AFN PILOT PLANT STEP I, REFRIGERATION		DRAWING NO.
DATE 5-12-60	DRAWN N. REGAN	APPROVED		PFS-265
SCALE —				

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This system had the advantage of using one refrigerant for three levels of refrigeration with the greatest part of the compressor loading occurring at the highest temperature. Figure 48 presents a detailed flow diagram of the system.

IV. Utilities

The utilities supplied to the plant and their location are given in the utility piping and instrumentation diagrams, Figures 49 and 50. As a safety precaution, breathing air fittings (Schraeder couplings), nitrogen and vacuum fittings (Snap-Tite connectors), and water and steam fittings (Chicago Pneumatic couplings) were different and used different hoses to prevent cross-connecting utility services. A list of the utilities provided the plant follows:

City Water

75 to 80 psig, 70°F. (max.)

Cooling Tower Water

64 psig, 280 gpm, 83°F. (max.)

Steam

175 psig (nominal)
40 psig

Natural Gas

30 psig

Nitrogen

75 psig

Caustic

Destruction Scrubber 40 psig,
85 gpm

Vacuum

Nash 25" Hg. Vacuum
Beach-Russ 5 mm. absolute

Refrigeration

-20°F., -50°F., -100°F.

Compressed Air

Instruments 60 psig, 69 SCFM, dew points 9°F. at 0 psig.
Plant Air 60 psig, 20 SCFM, dew point 20°F. at 0 psig.
Emergency 50 psig, 15 SCFM (from prepilot plant).

Electricity

Power: 440/220 V, 3-phase, 60 cycle, A.C., 236 K.W.
Two parallel feeders, 119 K.W. and 117 K.W.

Lighting: Two 15 KVA Transformers
480 V 3-phase/120-240 V, single-phase

Instruments: One 5 KVA Transformer
480 V 3-phase/120-240 V, single-phase

Emergency Lighting: Portable 2 lamp unit

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V. Equipment Specifications

A. Piping and Valves

In general, carbon steel tubing and piping were specified throughout the plant for process piping except where temperature conditions lower than -20°F. predominated. In these cases, type 304 stainless steel was used for process piping. Carbon steel, 0.065 inch wall, annealed, seamless tubing was used in only three sizes; 3/8 inch, 5/8 inch and 7/8 inch with carbon steel, cadmium plated Imperial Hi-Seal fittings. Carbon steel schedule 40 seamless Grade A/B ASTM A-53 pipe was used for one inch to six inch sizes with butt weld fittings. Flanges were used only where required for equipment removal and at control valves. The few screwed fittings required were 3000 pound forged steel.

Stainless steel 0.049 inch wall, seamless, type 304 with type 316 stainless steel Imperial Hi-Seal fittings were used for refrigerated process tubing in three sizes; 3/8 inch, 5/8 inch and 7/8 inch. Type 304 stainless steel schedule 10S seamless pipe was specified with schedule 10S butt welding type 304 stainless fittings in one inch to six inch sizes. Any required stainless screwed fittings were specified as 2000 pound type 304 stainless.

The valves specified for use in process tubing lines were Jamesbury screwed ball valves with Teflon seats and seals. For globe valve use, screwed steel body, union bonnet Kerotest N20A valves were used. A screwed stainless steel, spring loaded Durabla valve was specified for check valve service in process lines. Welding neck flanges with 1/16 inch raised face were specified for 300 pound and 150 pound service for use with Jamesbury flanged ball valves in one inch to six inch sizes.

For refrigerant lines, hard drawn copper tubing, ASTM B-68, Type L, was specified for use with brass valves and fittings. Refrigerant lines connected to threaded connections at equipment were connected using a silver alloy, back-brazed copper adapter.

For instrument air, nitrogen, and breathing air lines, schedule 40 galvanized, ASTM A-120 pipe and galvanized fittings were specified in 1/2 inch to 2 inch pipe sizes. Copper tubing, 1/4 inch with 0.030 inch wall and 12 tube bundles of Dekron Protecto Pac, type B, were also specified for instrument air lines less than 1/2 inch in size.

Other utilities, cooling water, plant water, steam, vacuum and chilled water under 125 psig and 350°F. used schedule 40 pipe ASTM A-53 Grade A/B with screwed 150 pound brass gate, globe, and check valves. Fittings were malleable iron 150 pound screwed. High pressure steam, 175 psig, and natural gas had 3000 pound fittings, 600 pound valves of forged steel, schedule 80 pipe for under one inch line size, and schedule 40 pipe for over one inch line size.

MIXED SO₂ SYSTEM

1E-19 DUTY: 46.6 M GPM/HR	1E-10 DUTY: 72.9 M GPM/HR	1E-5 DUTY: 40.1 M GPM/HR

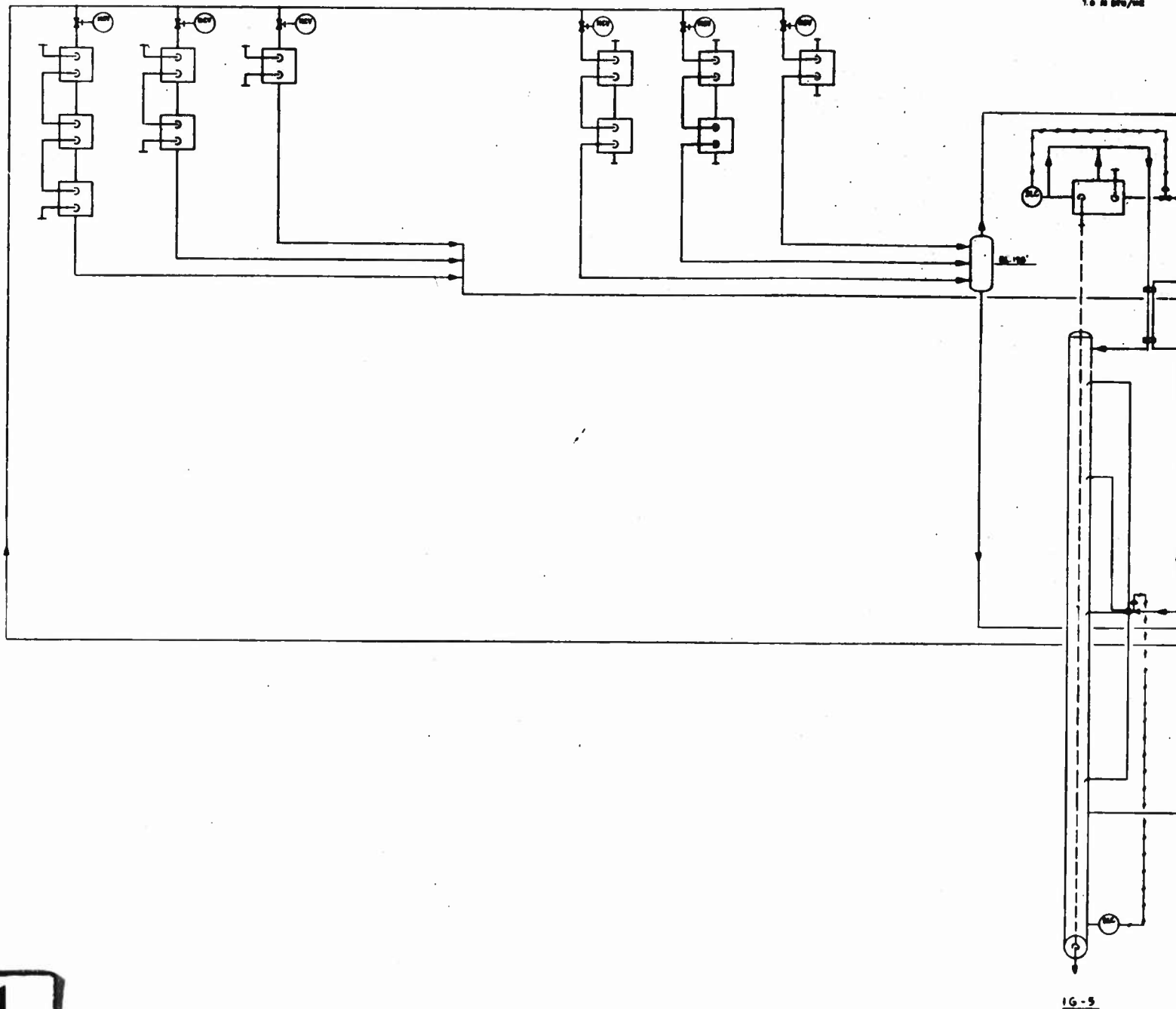
MIXED SO₂ SYSTEM

1E-11 DUTY: 10.7 M GPM/HR	1E-12 DUTY: 10.5 M GPM/HR	1E-21 DUTY: 5.2 M GPM/HR

SC-1
PHASE
SEPARATOR

1E-17
DUTY:
10.8 M GPM/HR

SE-1
PSS BR
SEPARATOR
DUTY:
7.0 M GPM/HR



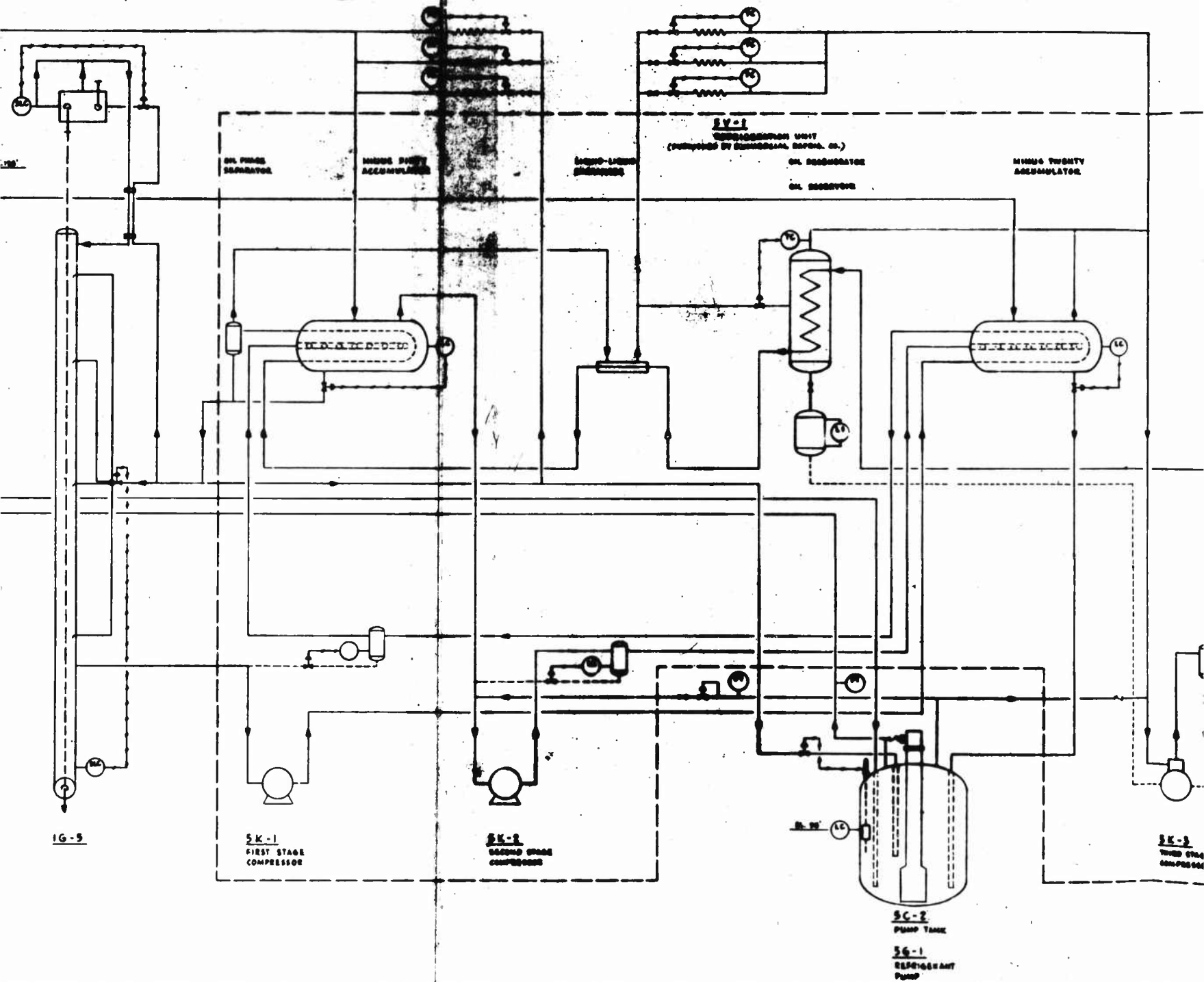
1

18-17
DVT
1.0 1000/10

58-1
DVT
1.0 1000/10

2

18-17
DVT
1.0 1000/10

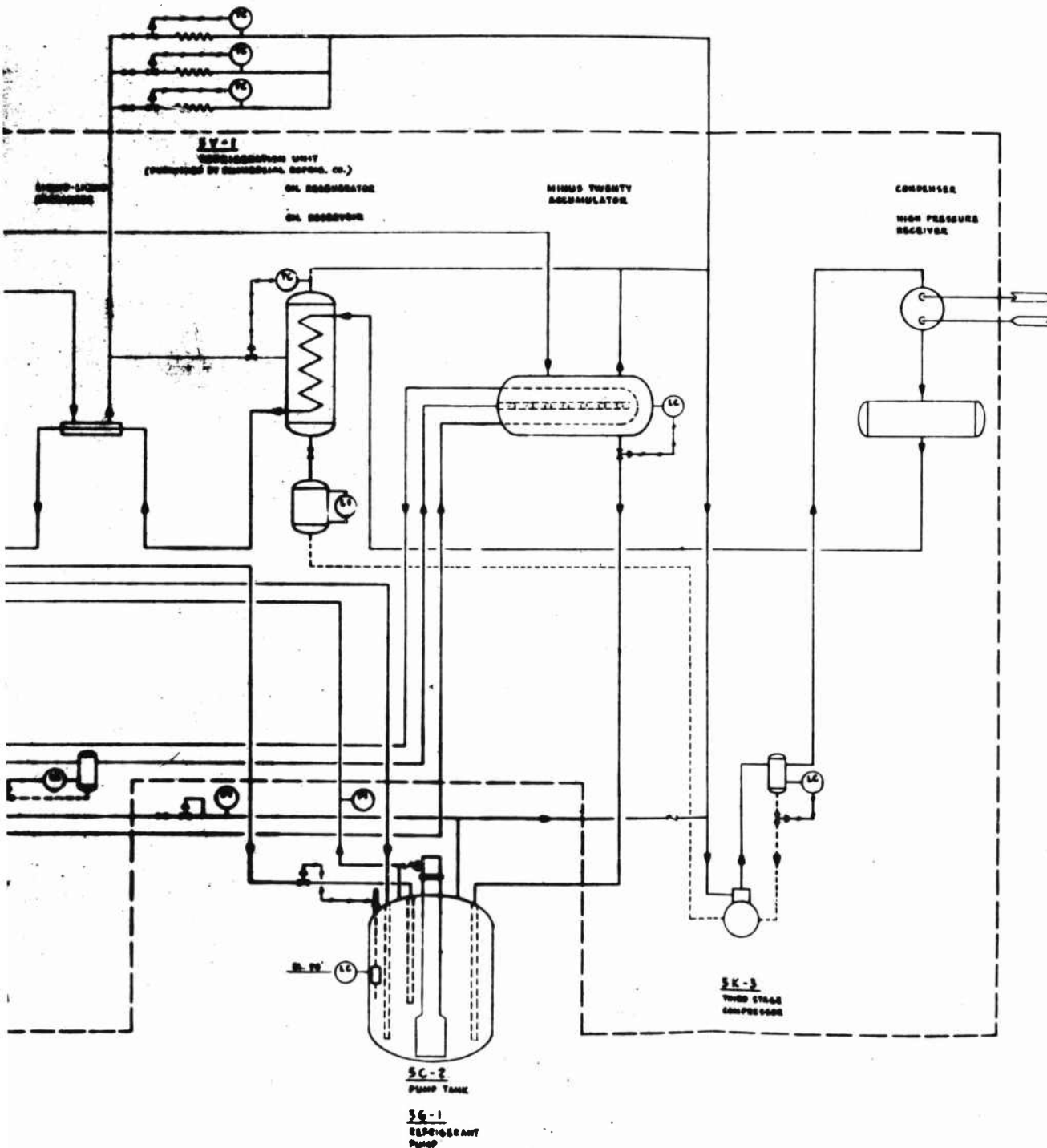


2000
THREE TWENTY
COPY:
S-6 4/20/48

NOTES

- 1 - PRESSURE TEMPERATURES AND CATALYTIC DATA BASED ON 2. ON CATALYTIC COMPOSITION AND 3. ON H₂ - O₂ RATIO. ACTUAL COMPOSITION TO BE SUPPLIED BY VENDOR.
- 2 - FLOW RATES ARE NOT DEPENDENT ONLY. OIL FLOW NOT INCLUDED.
- 3 - ALL QUANTITIES & DATA BASED ON 2-12 (H₂ - O₂ RATIO 2.0/1.0)

3



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PROCESS FLOW DIAGRAM STEP I - CATALYTIC HYDROGENATION THREE STAGE REFRIGERATION											
3192				5-RA-11							

IF-1 & IF-2
REACTOR FEED
HEATER AND
REACTOR

IV-1
FEED
FILTER
1/2" INSULATED 350°F

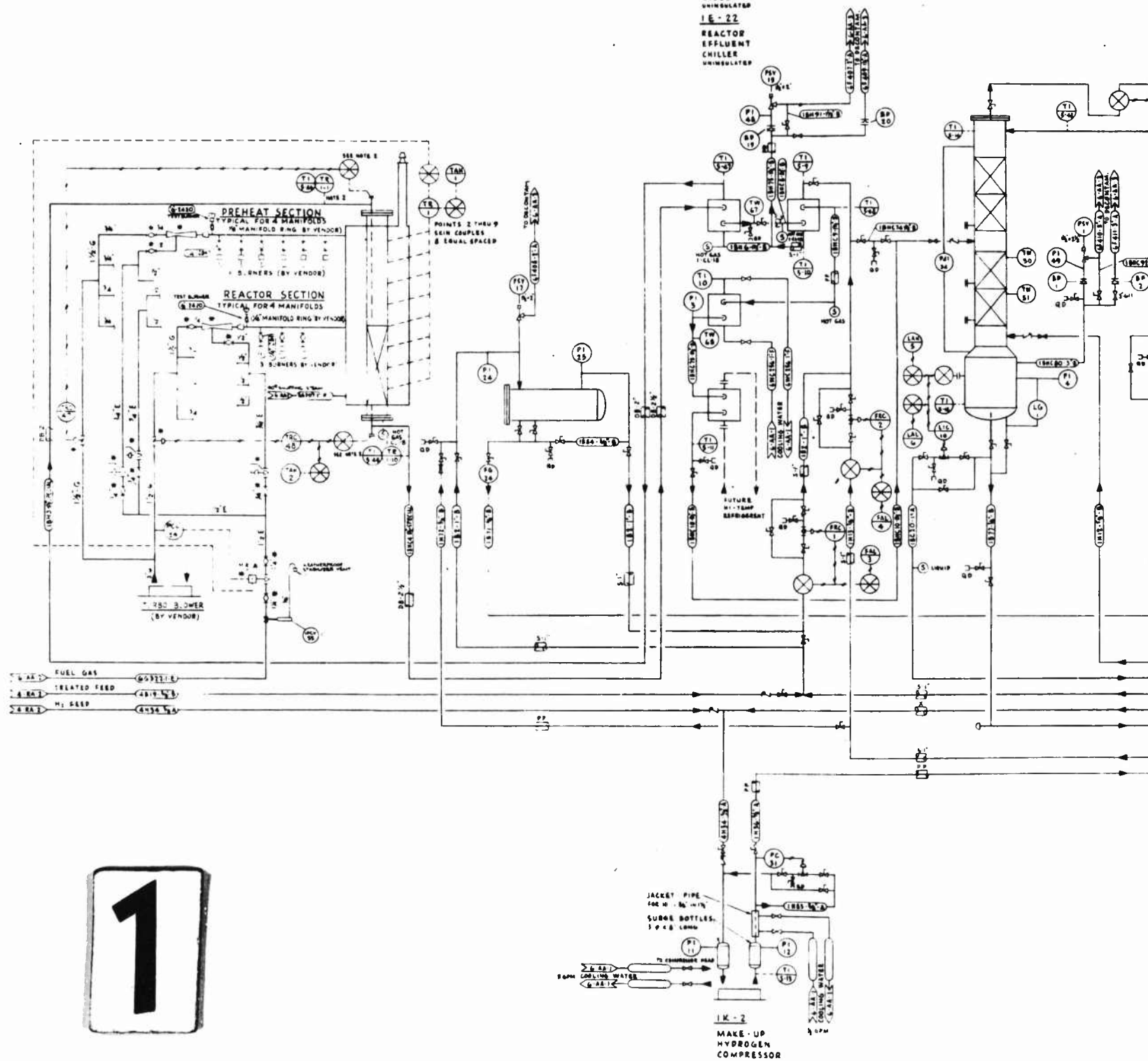
IE-1
REACTOR FEED
EFFLUENT
EXCHANGER
3" INSULATED 300°F

IE-2
FEED
VAPORIZER
1/2" INSULATED 400°F

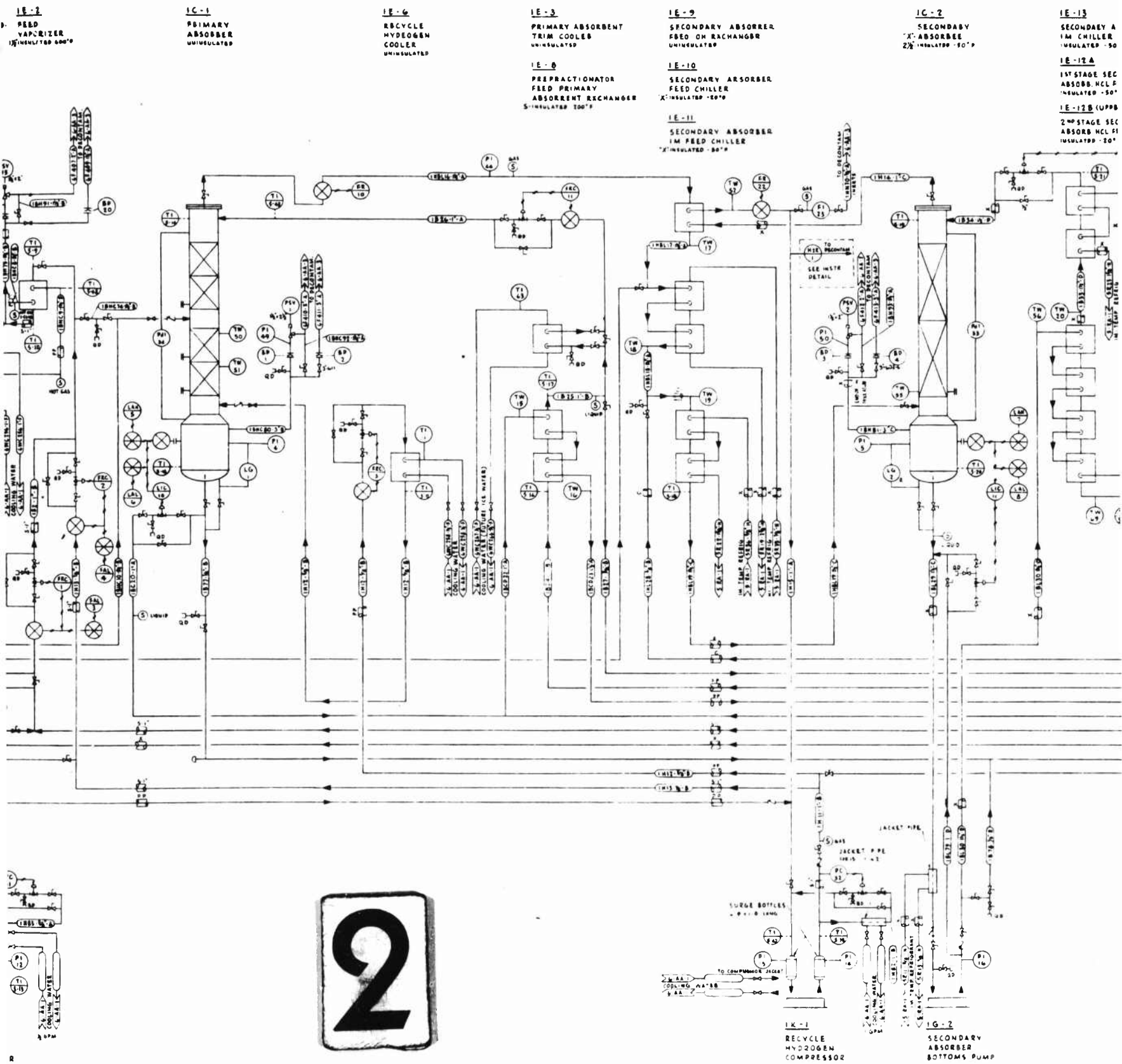
IC-1
PRIMARY
ABSORBER
UNINSULATED

IE-4
REACTOR
EFFLUENT
COOLER
UNINSULATED

IE-22
REACTOR
EFFLUENT
CHILLER
UNINSULATED



1



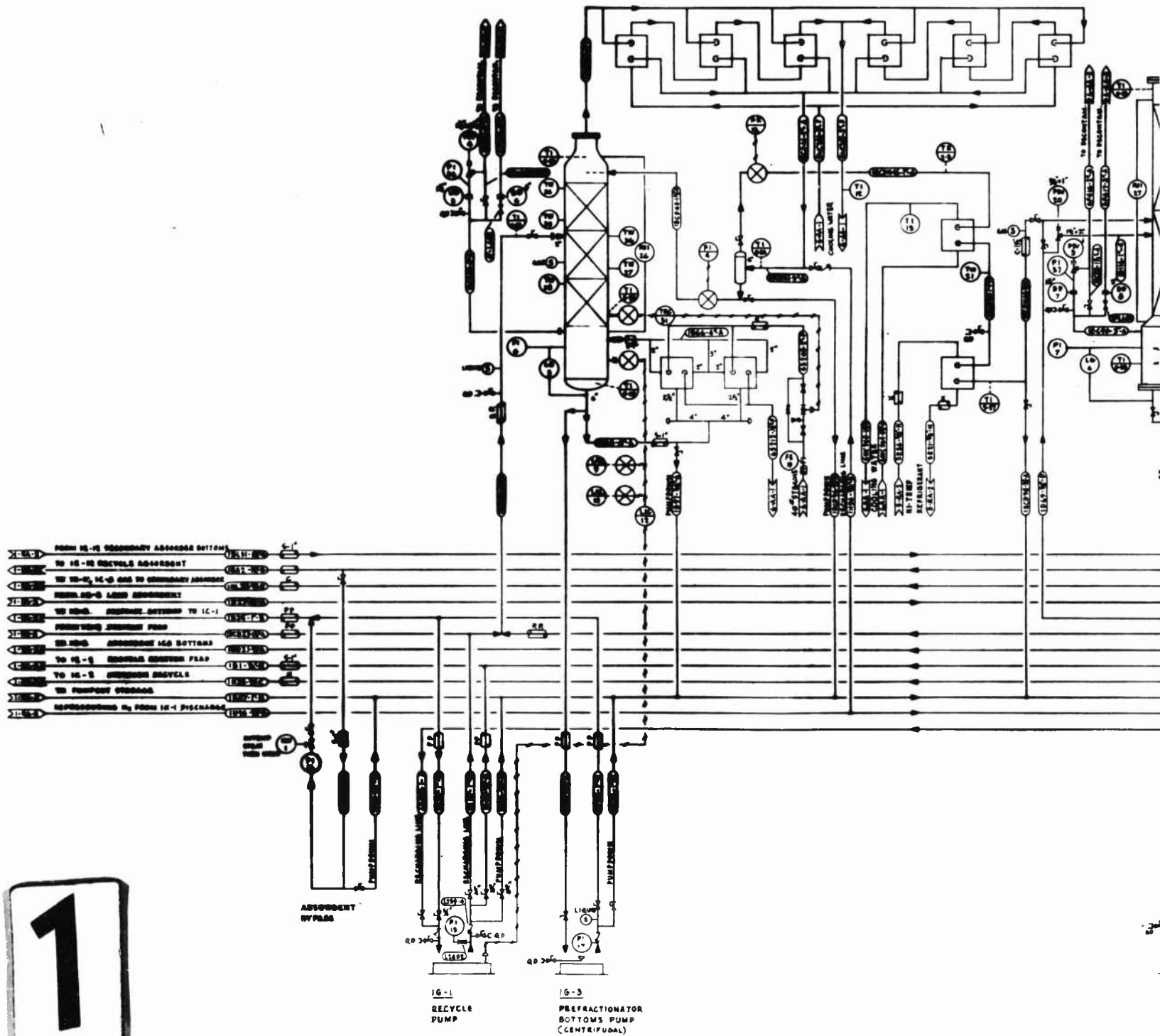
1E-2
PREFRACTIONATOR
5-1/2" INSULATE FOR 180°

1E-13
PREFRACTIONATOR
REBOILER
5-1/2" INSULATE FOR 180°

1E-14
PREFRACTIONATOR
O.H. CONDENSER
UNINSULATED

1E-7
DIS. FEED
COOLER
UNINSULATED

1E-5
DIS. FEED
CHILLER
7/8" INSULATE FOR -20°



1

1E-7
DIS. FEED
COOLER
UNINSULATED

1E-6
DIS. TOWER
"X" - INSULATE TOWER FOR -90°F
1½" - INSULATE KETTLE FOR R.P.

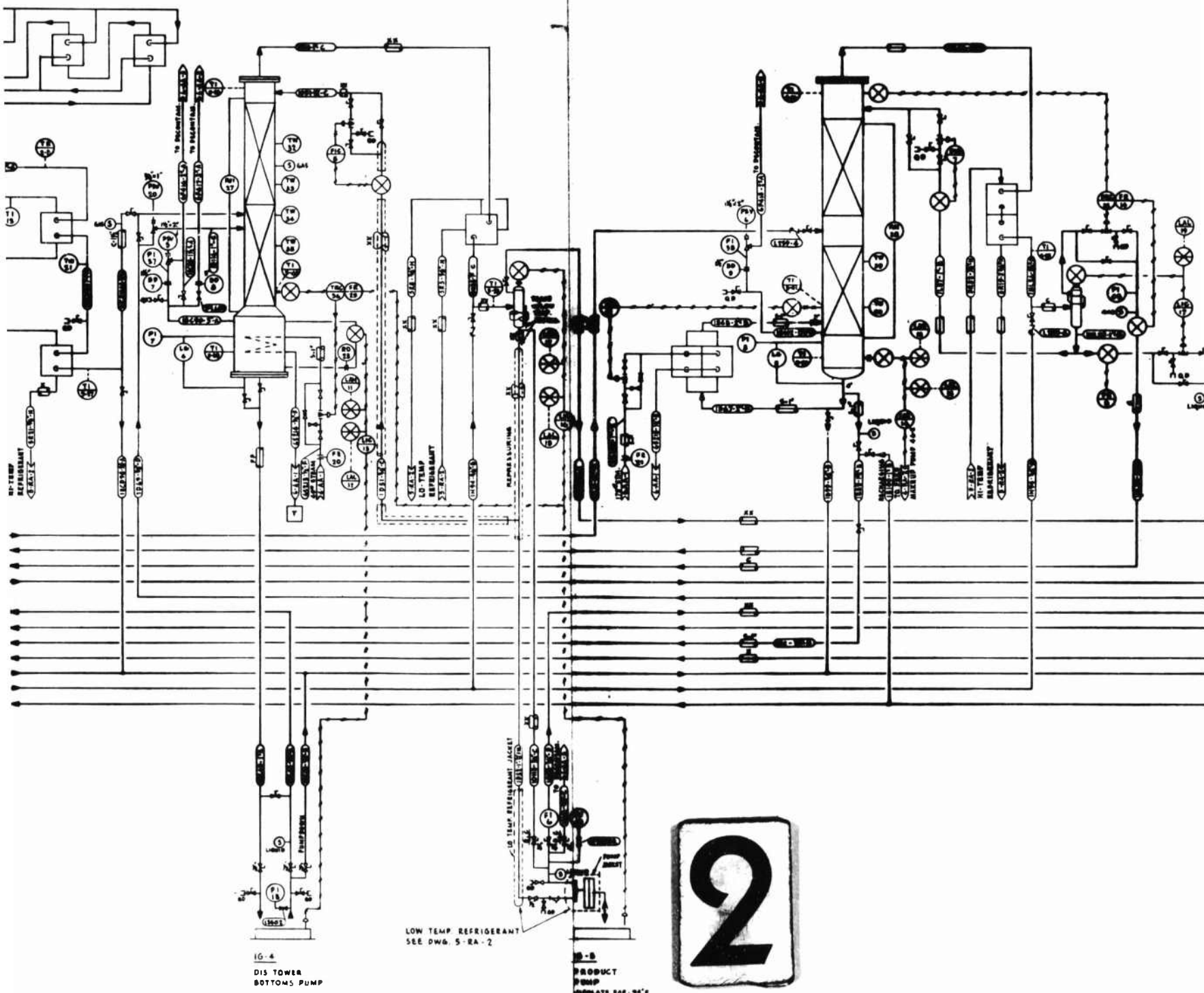
1E-17
DIS. TOWER
ON CONDENSER
3" - "X" - INSULATE FOR -90°F

1E-18
HCL FRACTIONATOR
REBOILER
5-1½" - INSULATE FOR 300°F

1C-5
HCL FRACTIONATOR
5-1½" - INSULATE TOWER TOP 1/3 FOR 15°F
4-1½" - INSULATE BALLANCE FOR 300°F

1E-19
HCL FRACTIONATOR
ON CONDENSER
(2½" - "X") - INSULATE FOR -90°F

1E-5
DIS. FEED
CHILLER
"X" - INSULATE FOR -90°F



2

OR
NEB. TOP 1/4 FOR 15°F
ALLANCE FOR 500°F

1E-19
HCL FRACTIONATOR
O H CONDENSER
(2 1/2" X) - INSULATE FOR -20°F

1E-20
FEED BOTTOMS
EXCHANGER
(2 1/2" X) - INSULATE FOR -20°F

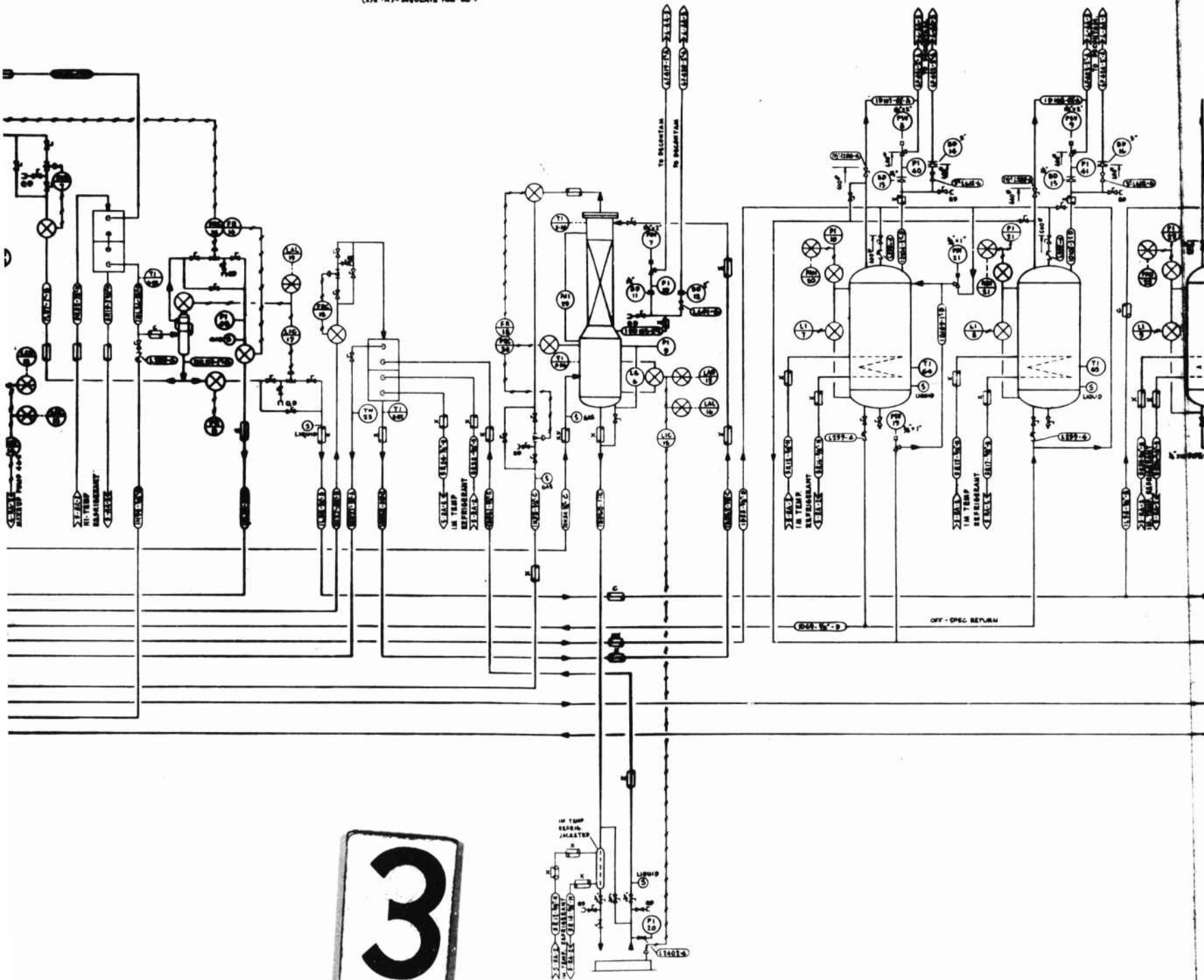
1E-21
D B ABSORBENT
CHILLER
(1 1/2" X) - INSULATE FOR -20°F

1C-8
D B ABSORBER
(2 1/2" X) INSULATE FOR -50°F

1C-7A
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

1C-7B
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

1C-7C
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

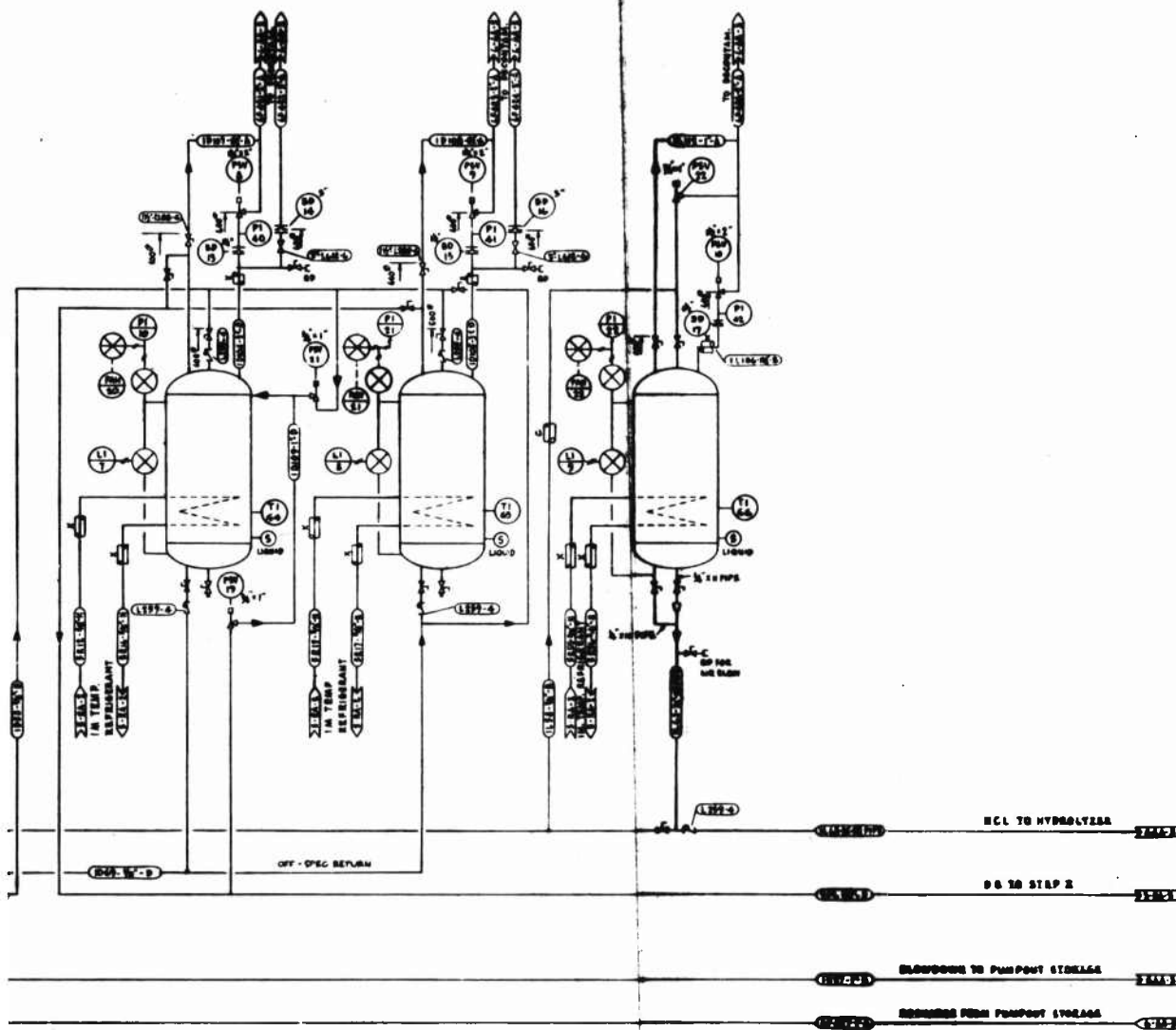


1G-6
D B ABSORBER
BOTTOMS
INSULATE FOR -50°F

IC-7A
DB STORAGE
(2 1/2" x) - INSULATE FOR -20°F

IC-7B
DB STORAGE
(2 1/2" x) - INSULATE FOR -20°F

IC-8
HCL STORAGE
(6 1/2" x) - INSULATE FOR -20°F



LEGEND									
PIPING SYMBOLS									
Gate Valve	Check Valve								
Ball Valve	Plug Valve								
3-Way Valve	Specialty Valve								
Open Disconnect	SS Sampling Valve								
Control Valve (Open on Air Failure)	Control Valve (Closed on Air Failure)								
Pressure Safety Valve	Steam Trap								
3 Way Plug Valve	Insulation (w/ Steam Trace)								
Insulation (w/ Steam Trace)	Insulation (w/ Steam Trace)								
INSTRUMENT SYMBOLS									
Local Mounted	To Admittance								
Board Mounted	Dead Weight Tester (Mounted on Pressure Section)								
Combination Indicator									
Pressure Line (W/ Steam)	Electrical Lead								
Instrument Control Air	Capillary Tubing								
INSTRUMENT IDENTIFICATION									
Plant Number	Instrument Identification								
Instrument Number									
ALL INSTRUMENTS ARE CODED IN ACCORDANCE WITH THE I.S.A. STANDARDS EXCEPT AS NOTED.									
LINE IDENTIFICATION									
Line Number									
Piping Specification									
Line Size									
Serial Number									
Commodity or Service									
Plant Number									
COMMODITY DESIGNATION									
NOTES									
1 - ALL LOW POINTS IN PIPING AND EQUIPMENT REQUIRES 90 DEGREE CONNECTIONS. SLOPE ALL PROCESS LINES AND AVOID ALL LOW POINTS AND ELIMINATE ALL DEAD ENDS POSSIBLE.									
<table border="1"> <tr> <td>DATE</td> <td>REVISION</td> <td>BY</td> <td>CHKD</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> </tr> </table>		DATE	REVISION	BY	CHKD				
DATE	REVISION	BY	CHKD						
HCL TO HYDROLYZER DB TO STEP 2 DISCHARGE TO PUMPOUT STORAGE RECOVERED FROM PUMPOUT STORAGE									
4									
3192 1-RA-43									

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In addition, specifications for process piping called for 1/12 inch per foot slope in direction of flow for draining. Teflon tape was specified as thread lubricant for stainless threaded connections and Garlock 101 for carbon steel threaded connections.

B. Columns and Vessels

All vessels were constructed in accordance with ASME code specifications for unfired pressure vessels and had been tested to withstand pressures of one and one-half times design rating. Except for five stainless steel columns and vessels, all are of carbon steel. The five stainless steel vessels made of type 304 stainless were the secondary absorber (1C-2), the top section of the disproportionator (1C-3), the diborane storage tanks (1C-7A, -7B), and the diborane absorber (1C-8). A corrosion allowance of 1/8 inch was used for the carbon steel equipment and 1/16 inch for the stainless equipment.

Generous allowances were made for design pressure ratings for equipment normally operated at low pressures, 10 to 75 psig. As a minimum standard for these, a design rating of 150 psig was used for columns, 100 psig for storage vessels.

C. Heat Exchangers

Except for the reactor feed-effluent exchanger (1E-1) made of silver lined Inconel and the diborane absorber chiller (1E-21) made of stainless steel, the heat exchangers in the pilot plant were carbon steel. Most exchangers were Griscom-Russell extended surface finned heat exchangers except in cases where a double pipe exchanger could be fabricated in the field for small loads.

D. Pumps and Compressors

Several types of pumps and compressors were utilized in the plant. Positive displacement diaphragm type pumps were used for low volume, high pressure service or for low volume constant feed service. An example is the diborane product pump (1G-5) used to transfer liquid diborane. This type of pump was used primarily to eliminate the need of packing or seals on rotary or reciprocating shafts. A compressor used for hydrogen recycle (1K-2) was also of the diaphragm type. It was installed in the plant to compare its service to that of a Worthington reciprocating, non-lubricated, carbon ring packing compressor also used on hydrogen service (1K-1).

Normal process transfer of BCl_3 was accomplished with both centrifugal and turbine type pumps depending on pressure differential and load required. These pumps were equipped with single mechanical seals backed up with a close fitting carbon throttle bushing to prevent excess leakage in case of seal failure. Double mechanical seals were not used in these pumps because no satisfactory seal fluid was available. Conventional packing was out of the question because operating pressures were over 100 psig.

C O N F I D E N T I A L

VI. Waste Disposal

Disposal of waste material in the AFN pilot plant consisted mainly of process waste gas disposal and process solids disposal.

A caustic scrubber normally containing 500 gallons of 5 per cent caustic solution was used to destroy boron compounds in any vented gases. The scrubbing tower was 24 inches in diameter and contained six plates. All rupture discs and safety relief valves in the process vessels of the plant were manifolded to release their vapors to this scrubber in case of pressure build-up. To prevent back inspiration of air into the system during normal operation, natural gas was constantly bled into the ends of the gas manifold. To prevent air inspiration after a rupture disc or safety relief valve had opened, a gas pressure control valve released natural gas into the manifold system when manifold pressure dropped below 4 inches of water above atmospheric pressure. A caustic solution pump circulated 40 to 60 gpm to the scrubber and was also used to provide caustic solution for clean out of equipment in the pilot plant.

The solids waste in the plant may consist of boron hydrides and/or boric acid fouling equipment. Caustic solution from the scrubber was used to clean out solids from fouled equipment.

Solids which were found in dismantling equipment which had not been removed by a caustic wash were inerted by decontaminating the equipment with 2.5 per cent ammonia solution. The ammonia solution was made available in the plant in several loosely covered 55-gallon drums and used for personnel decontamination, equipment decontamination, and for washing down process liquor spills.

VII. Operating Procedures and Philosophy

Operating instructions for the pilot plant are detailed in Appendix J. However, a more general explanation of the procedures, underlying philosophy, and equipment selection is presented here. Instrument and equipment designations mentioned in the text can be identified by reference to the piping and instrument diagrams, Appendix I.

A. General Controls

Flow controller FRC-2 sets the hydrogen feed rate to the reactor through exchangers IE-2 and 1E-1; flow controller FRC-3 sets the hydrogen flow rate for stripping gas to the primary absorber (1C-1). Make-up hydrogen is measured in flowmeter 4FR-6 and is pumped into the process by hydrogen compressor (1K-1) as the process requirements demand. The system's need for additional hydrogen is indicated by a lowered suction pressure to this compressor; a pressure regulator in the make-up hydrogen supply line then acts to hold this pressure constant by admitting hydrogen to the process from the supply trailer.

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Flow controller FRC-1 in the BCl_3 feed line to exchangers 1E-2, 1E-1 and furnace 1F-1, sets the BCl_3 flow to the reactor. Make-up BCl_3 is measured by change in liquid level of the BCl_3 storage tank (4C-4A, B or C) plus a crosscheck with flow recorder FR-8. Rotameter FI-7 in the BCl_3 feed pump (4G-2) discharge line determines only if flows exist. Boron trichloride is fed as make-up into the system as called for by the bottoms liquid level controller (LIC-14) on hydrogen chloride fractionator (1C-5). This controller determines the make-up pump's rate.

A bleed of recycle H_2 may be taken from the system from the secondary absorber (1C-2) overhead stream. A small, constant flow from this source passes through a continuous H_2 thermal conductivity monitor ($\text{H}_2\text{R-1}$). If the H_2 concentration drops to less than 95 per cent, an additional bleed stream can be taken through flow meter FI-23 and into the gas destruction header to clear the system of inerts.

The three major pressure levels in the plant are controlled separately. Pressure controller PRC-30 in the overhead line of diborane absorber (1C-8) sets the pressure in this column, the disproportionator (1C-4), and prefractionator (1C-3). Back pressure controller PRC-35 in the overhead line from the HCl fractionator sets the pressure in this unit. The pressure in the reactor (1F-1,2), the primary absorber (1C-1) and secondary absorber (1C-2) is set by the pressure controller PC-31 on the discharge of the H_2 make-up compressor which is tantamount to the suction of the recycle compressor (1K-1). In addition, the pressure controller PC-31 on the H_2 recycle compressor (1K-1) is set at 231 psig to overcome pressure drop through the flow control system, reactor and absorbers, and the suction pressure to the make-up H_2 compressor (1K-1) is controlled as previously described.

Production of liquid diborane product is measured by change in liquid level of the storage vessels (1C-7A, -7B) with flow meter FI-6 in B_2H_6 product pump (1G-5) discharge line giving a general flow indication. By-product HCl is stored in vessel 1C-9 and is also measured by change in liquid level. A crosscheck on the material balance for HCl production is also obtained by flowmeter FR-8 in the product take-off line from the HCl fractionator (1C-5).

B. Start-Up Procedure

The plant is initially filled with clean, dry hydrogen at approximately 10 psig (H_2 compressors 1K-1 and 1K-2 are bypassed to fill the plant with H_2 directly from supply trailer).

A working level of BCl_3 is established in the various columns by filling from the BCl_3 storage tanks (1C-4A, B and C) in the Step IV area. Further BCl_3 additions are made as necessary with the make-up pump (4G-2) on automatic control (LIC-14).

Hydrogen pressure in the system is increased to 40 psig (temporarily bypass H_2 compressors 1K-1 and 1K-2).

C O N F I D E N T I A L

During normal operation, liquid BCl_3 is transferred by column pressure, established at 300 psig by PRC-35, from the bottom of the HCl fractionator (1C-5) to the reactor (1F-1, -2). Before the HCl fractionator is in operation, however, there is no pressure differential available for this transfer. The fractionator is placed in operation at total reflux. Although reflux is not expected at this point, refrigerant is started to the overhead condenser and flow controls set for total reflux with the overhead take-off valved off. Steam is then started to the reboiler manually. The prefractionator (1C-3) and the disproportionator (1C-4) are next placed into operation at total reflux in a similar manner with the pressure controller on the diborane absorber (1C-8) set at the desired pressure of 72 psig.

Operating pressure in the HCl fractionator (1C-5) is supplied by the H_2 compressors (1K-1 and 1K-2) through the repressuring line which is opened momentarily for this purpose. Since liquid circulation through the secondary absorber (1C-2) cannot be established until the HCl fractionator (1C-5) is pressured, chilled liquid is not available to desaturate the H_2 recycle stream. Circulating warm H_2 saturated with BCl_3 might drop out liquid in the compressor. For this reason H_2 circulation should be stopped by closing the valves at 1FRC-2 and 1FRC-3.

When the HCl fractionator (1C-5) has been pressured to 231 psig (output pressure of 1K-1), the compressors (1K-1 and 1K-2) are shut down. Liquid circulation between the secondary absorber (1C-2) and the fractionator (1C-5) is established by starting the secondary absorber bottoms pump (1C-2) and setting 1FRC-9 at flow rate of 4102 lbs./hr. Boron trichloride recycle of feed from the fractionator (1C-5) to the reactor (1F-1, 1F-2) is prevented by keeping the valve at 1FRC-1 closed.

As soon as the secondary absorber (1C-2) is cooled to operating temperature (-45°F.), the compressors (1K-1 and 1K-2) can be restarted. The valves at 1FRC-2 and 1FRC-3 should be opened to permit H_2 circulation through the furnace-reactor (1F-1 and 1F-2), and the primary and secondary absorbers (1C-1 and 1C-2).

Liquid BCl_3 circulation is then established in the remainder of Step I, excluding the furnace-reactor (1F-1, 1F-2) and exchangers (1E-1, 1E-2, 1E-4 and 1E-22). This is accomplished by starting the prefractionator bottoms pump (1C-3) and setting the absorbent rates to the primary absorber (1C-1) and the B_2H_6 absorber (1C-8) by means of 1FRC-11 and 1FRC-15, respectively. The B_2H_6 absorber bottoms pump (1C-6) is also turned on automatic operation.

The furnace-reactor section of the plant is operated at the high temperature level of 1300°F. and contains silver screen for catalyst and as equipment lining for corrosion protection. Design heat transfer rates are very high in this section, and it is imperative that flow be maintained through the equipment while it is being fired to prevent melting of the silver catalyst and lining. Furthermore, BCl_3 without H_2 present is very corrosive at these temperatures. It is therefore very important that H_2 flow be established first and stopped last. It is also essential to avoid

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putting the reactor under a vacuum which might pull the silver lining loose from its substrate.

After a steady H_2 flow of 49 lbs./hr. is set at FRC-2, the furnace temperature controllers (1TRC-47 and 1TRC-48) are set at 1000°F. and the individual burners lit. When furnace-reactor temperatures reach 800°F. (1TI-5-44,45) the temperature controllers are inched up gradually until a reactor temperature of over 1000°F. is indicated. The controllers are then set at the desired operating temperature, 1300°F., and BCl_3 flow started through the reactor at a minimum rate by the use of flow controller (1FRC-3). This additional heat load slows down the heating rate. However, the BCl_3 flow rate can be gradually increased until the desired rate, 955 lbs./hr., is achieved at the design reactor temperature. It is necessary to turn on the BCl_3 recycle pump (1G-1) to achieve this rate.

When liquid and gas feeds to the reactor are steady and the furnace-reactor is up to temperature, the skin temperatures (1TR-1) of the reactor should be checked. It may be necessary to adjust the burner trim valves at this time in the event of high or uneven skin temperatures.

After the reactor starts operating and dichloroborane accumulates in the system, the flow rate of overhead vapor from the prefractionator to the disproportionator will increase (1FR-12) above the low rate expected from just dissolved H_2 in BCl_3 . Then, as B_2H_6 accumulates in the disproportionator overhead, the temperatures of the top of the column (1C-4) will drop to the design temperature of -70°F. (at 76 psig). When the disproportionator overhead temperature (1 TI-5-26) and reflux rate (1FIC-5) indicate that pure B_2H_6 is being produced, B_2H_6 product take-off to one of the refrigerated storage tanks (1C-7A and 1C-7B) should be initiated by starting product pump (1G-5). Rate of pumping is controlled by level controller LIC-16 on the accumulator.

Furnace operation also produces HCl. As HCl accumulates in the HCl fractionator overhead, the overhead temperature drops. Again, when the overhead temperature (1 TI-5-31) and the reflux rate (1FIC-7) indicate that pure HCl is being produced, take-off to the storage tank (1C-9) can be started. Take-off rate is controlled by the reflux accumulator level controller (1 LIC-17).

After final adjustments to operating variables, and waiting for the system to come to equilibrium, the plant should be in normal operation.

C. Shutdown Procedures

Because the hydrogenation reactor (1F-1, 1F-2) is susceptible to costly damage if overheated, it is important that shutdown operations are carried out in the proper sequence.

1. Shut off all gas to burners.
2. After reactor temperature begins to drop, gradually reduce BCl_3 feed (1FRC-1) to zero.

C O N F I D E N T I A L

3. Shut off H_2 feed only after reactor temperature as indicated on 1TRC-1 is below $500^\circ F$.
4. Isolate reactor from remainder of system.

Operation of the remainder of the plant must be continued for several hours until all available B_2H_6 and HCl are removed from the system to storage. At that time the steam to the reboilers is shut off, all liquid flows stopped, and the pumps turned off. The compressors (1K-1, 1K-2) are stopped and the plant is bottled up. Finally, the refrigeration system is put on "pumpdown" to remove all refrigerant from the entire system to the receiver. The B_2H_6 and HCl storage tanks, however, are kept cold continuously by the auxiliary refrigeration unit. The destruction scrubber pump, the cooling tower and pump, and the plant air compressor also operate constantly.

For safety reasons, a close surveillance over the plant should be maintained for several hours after it is shut down. As various parts of the plant approach ambient temperature from their normal operating temperature, leaks may develop or pressures may rise due to volatilization of condensed liquids. These problems can be readily handled by knowledgeable personnel.

D. Boron Trichloride Feed Preparation

Purification of the BCl_3 supply is accomplished by batch distillation. First, most of the phosgene is removed in an overhead cut, and then the purified feed is taken off overhead to storage, leaving heavy materials in the bottoms. Since these are originally present in low concentration, they may be accumulated in the still pot for several batches before being disposed of. The separation of phosgene from BCl_3 is very difficult and a high reflux ratio of 45:1 is required for the first cut. The product cut can be taken off at a 1:1 reflux ratio.

The BCl_3 , received by tank car, is first transferred to storage cylinders which hold approximately 1600 pounds each. These are transported by fork lift truck to the weigh scale (4V-2). Nitrogen pressure is then used to transfer a weighed batch of 2500 pounds to the distillation column (4C-2A) from two or more cylinders. The column is started up on total reflux, venting as necessary from the top of the reflux accumulator to establish an operating pressure of 50 psig, until steady state conditions are reached. Then the phosgene cut is taken off at a slow rate to a cylinder on the weigh scale until the phosgene concentration in the column is low enough to give a product containing less than 0.10 per cent. Overhead take-off is then switched to one of the storage tanks (4C-4A, B or C) and take-off rate increased to 600 pounds per hour. Take-off is continued until the full charge is distilled over, but checking column temperatures to insure a pure product. Material balance information is provided by the weight readings and changes in levels of the column and storage tanks.

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Periodically the accumulated phosgene cuts can be recharged to the distillation column and concentrated further to recover much of the BCl_3 removed with the phosgene. Eventually the concentrated waste cut is sewerred with a large excess of water. Similarly the concentrated bottoms, which contain carbon tetrachloride, silicon tetrachloride and perhaps solids, are periodically removed to a storage bottle and then flushed down the sewer with excess water.

PILOT PLANT OPERATIONS

I. Preparations

Much of the preparatory work toward operation of the pilot plant had been completed when the diborane unit (Step I), constructed by Bechtel Corporation, was officially accepted by American Potash & Chemical Corporation in mid August, 1960. Operating and analytical personnel had been assigned and familiarized with the details of the process, equipment and procedures in a training program begun three months earlier; columns had been packed; much of the equipment had been cleaned and drying was in progress; process and analytical instruments were checked and calibrated; some BCl_3 feed had been distilled; and protective and emergency safety measures had been developed and reviewed. Upon acceptance of the plant, the major activities remaining prior to start-up were the completion of the equipment washing and drying and the test operation of the pumps, compressors, and other plant elements. These were completed by the end of the first week in September, 1960.

Each operating shift was supervised by an experienced engineer. Assisting him in the operation of the plant were a junior engineer and a research technician. (Later, the junior engineer was released for other work and replaced by a second technician.) A chemist and laboratory technician on each shift furnished analytical support. Three such crews operated the plant for ten consecutive days and then had four consecutive days off to complete the two week period. The pyrolysis unit (Step II) was operated alternately with the diborane unit (Step I), thus providing time for maintenance, checks, and minor modifications between runs. A one man safety surveillance was maintained over the pilot plant during idle periods.

II. Raw Materials

As shown in Table 54, the BCl_3 available for use in the pilot plant contained phosgene and lesser amounts of chlorine, silicon, sulfur dioxide, and carbon tetrachloride. Prepilot plant investigations indicated that high purity BCl_3 was required; otherwise, impurities could lead to deterioration in the reactor of the silver screen catalyst and plugging of

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the reactor with solids. Although complete elimination of these impurities was not feasible, it was possible to reduce the phosgene and carbon tetrachloride levels in the Air Force BCl_3 to a reasonable level and filter the various process streams to remove any solids which might form.

TABLE 54

Typical Analyses of Boron Trichloride as Received

	AFN Specifications	Air Force BCl_3	Trona BCl_3
COCl_2 (mole %)	< 0.1	0.33	0.05
CCl_4 (mole %)	Nil	0.20	None Found
Cl_2 (ppm)	< 1,000	180	120
Si (ppm)	< 300	93	180
SO_2 (ppm)	Nil	50	None Found

The BCl_3 purification system, shown in Figure 46, was designed to operate on a batch basis, taking a topping cut of phosgene, chlorine and sulfur dioxide with a small amount of BCl_3 first, then taking the refined BCl_3 off as a second overhead cut, leaving any high boiling impurities in the bottoms. At the beginning of each batch, the fractionating column (4C-2A) was operated under total reflux to obtain a high concentration of phosgene, etc. at the top of the column. The best results were obtained by intermittent removal of the phosgene-containing overhead cut between periods of total reflux rather than by continuous take-off as originally designed.

The start-up and operation of the purification system proceeded with only minor difficulties. In July, 1960 two batches of the BCl_3 received from the Air Force were distilled to produce 3,000 pounds of purified feed stock. Analyses and material balances for these batches are given in Tables 55 and 56, respectively. The overhead products were highly satisfactory; the phosgene contents of 0.073 and 0.036 mole per cent were well below the maximum specification value of 0.1 mole per cent.

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BCl₃ Feed Analyses

	Batch 1	Batch 2
COCl ₂ (mole %)	0.073	0.036
CCl ₄ (mole %)	Nil	Nil
Si (ppm)	7.8	3.0
Cl:B Ratio	3.00	3.07
BCl ₃ (Wt. %)	100	100

BCl₃ Distillation Material Balances

	Batch 1 (lbs.)	Batch 2 (lbs.)
<u>In</u>		
Heel from Previous Batch	None	1160 ^(a)
Weight Charged from Cylinder	<u>3475</u>	<u>1595</u>
Total	3475	2755
<u>Out</u>		
Phosgene Cut	345	230
Purified BCl ₃ Cut	1705	1890
Heel Left in 4C-2A	490	590
Unaccounted For	<u>935</u> ^(b)	<u>45</u> ^(c)
Total	3475	2755

- (a) Heel greater than indicated from Batch 1 because of calibration tests carried out.
- (b) Estimated breakdown of losses:
- | | |
|--|-----------------|
| Improper venting at start of run | 500 lbs. |
| Fill system and clear plugs | 145 lbs. |
| Vent losses during COCl_2 and BCl_3 cuts | <u>290 lbs.</u> |
| | 935 lbs. |
- (c) Vent losses while eliminating N_2 from system.

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Four more batches were distilled in August, providing an additional 10,700 pounds of purified feed material. Table 57 presents the material balance information for these batches.

TABLE 57

Material Balance BCl₃ Distillations, Step IV

Batch No.	Fresh Charge (lbs.)	Waste Cut (lbs.)	Product Cut (lbs.)	Column Bottoms Gain (+) Loss (-) (lbs.)	Net Gain (+) or Loss (-) (lbs.)
3	2,818 (AF)	283 ^(a)	2,847	-272	+ 40
4	2,942 (TRONA)	0	1,862	+ 969	-111
5	1,788 (TRONA)	0	2,006	-334	-116
5 ^h	0	222 ^(b)	884	-996	+ 110
6	<u>3,502</u> (TRONA)	<u>0</u>	<u>3,133</u>	<u>+ 352</u>	<u>-7</u>
Totals	11,050	505	10,732	-271	-84

(a) COCl₂ cut.

(b) Bottoms accumulation in distillation since start of operation was sewerred because it was high in solids and high boiling impurities.

Batch No. 3 utilized the BCl₃ received from the Air Force; a phosgene cut was removed as on the first two batches described above. Again the technique of intermittent tops removal between periods of total reflux was required to achieve the best separation in the column. At this point the tops contained 6.1 per cent COCl₂ while the bottoms contained 0.13 per cent (the original Air Force BCl₃ contained 0.33% COCl₂). A 116 pound cut was quickly taken off and the column put back on total reflux; subsequently two additional cuts were made in a like manner to bring the total phosgene cut to 283 pounds. The final product was then taken off; a sample from the receiver analyzed 0.014 per cent COCl₂, no Cl₂ or CCl₄, and one ppm Si. A very pure feed material was thus obtained.

Batches 4, 5 and 6 utilized TRONA BCl₃; no COCl₂ cuts were required since this material already meets the 0.1 per cent maximum specification for phosgene. No problems were encountered in running these batches, although the "heel" left in the column after Batch 5 was discarded because high boiling impurities had reached a high concentration (CCl₄, 10.0 mole per cent; Si, 800 ppm by wt.). Nevertheless, the column still made a satisfactory separation.

Throughout these batches a considerable amount of hand venting was required to maintain the column pressure at a reasonable level. Since this was necessarily done intermittently, minor upsets in the operation

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were experienced. To alleviate this condition, a pressure regulator was installed on the vent line. Table 57 indicates that the vent losses over a number of batches were reasonable, despite some apparently substantial losses on individual batches. The variation in vent losses from batch to batch can probably be explained by the number of readings required to make a material balance (Batch No. 3, for example, involved six weighings and five level readings), coupled with differences in the extent to which the column drains before a final level reading on the bottoms is obtained.

No difficulties were encountered in subsequent operation of the purification unit which was carried out routinely as required. In general, TRONA boron trichloride was used as feed material without purification. No evidence of increased solids formation or poisoning of the silver catalyst was evidenced.

Since all hydrogen used met the purchase specifications, no purification of this raw material was required.

III. Experimental Results

A total of sixteen runs were made in Step I. The first started on September 8, 1960 and Run 16 ended January 29, 1962. The pertinent data from these runs have been summarized in Table 58. Several important conclusions are apparent from examination of the data in Table 58:

1. The process is capable of producing B_2H_6 of greater than 99 per cent purity (Ref. Runs 2,3,7). HCl was the major impurity and its occurrence is discussed in more detail later in the report. In some runs, BCl_3 and $BHCl_2$ appeared as impurities, but this is attributed to improper operation of the disproportionator (1C-4 in Fig. 45). The fact that these compounds were usually absent indicates that this column was capable of making a good separation.
2. Hydrogen chloride was also produced in high purity (Ref. Runs 2, 3, 5, 7, 9, 13, 15, 16). Although B_2H_6 was an impurity in some of the earlier runs, only BCl_3 showed up in the later ones. An equipment change was responsible for the disappearance of B_2H_6 . Again, improper operation of the HCl fractionator (1C-5) caused BCl_3 contamination. In some runs, considerable emphasis was placed on producing a hydrogen chloride-free bottoms from this column, and this was accomplished at the expense of boron trichloride overhead occasionally. However, this straightforward physical separation can be made to whatever degree desired by an appropriate distillation column.

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TABLE 58

PILOT PLANT RUN SUMMARY

DESIGN CONDITIONS	Total Run Time (h.-s.)		Total Reactor Run Time (h.-s.)		Average Reactor Temp. (°F.)		Avg. BCl ₃ Feed Rate (lb./h.-s.)		Avg. H ₂ /BCl ₃ Ratio (mole-%)		Avg. Conversion Rate (%/Pass)		Total BHC1 ₂ Produced (as lb. B ₂ H ₆)		Total B ₂ H ₆ Recovered (as lb. B ₂ H ₆)		Total HCl Recovered (as lb. B ₂ H ₆)		Yield Based on Make-up BCl ₃		Yield Based on Make-up H ₂		Yield Based on BHC1 ₂ Produced		DIBORANE PRODUCT ANALYSES						PRODUCT		
	Run	Date											% B ₂ H ₆	% HCl	% B ₂ H ₆	% HCl	% B ₂ H ₆	% B ₂ H ₆	% BCl ₃	% Mole % BHC1 ₂	% Mole % HCl	% Mole % HCl	% Mole % HCl	% Mole % HCl	% Mole % HCl	% Mole % HCl	% Mole % HCl	% Mole % HCl					
DESIGN CONDITIONS			1290	955	3 0/1	20.0		7 51b/hr	52.4b/hr	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100			
1 Sept. 8 9, 1960	27	24	1090	630	3 3/1	7.4	44.0	0		0	0	0	0	0	0	0	0	0	99.6	Nil	0.4	N.D.	100	Nil									
2 Oct. 5 8, 1960	80	73	1140	660	2 2/1	18.3	348.0	13.5	27.0	12.4	25.7	6.8	14.1	3.9	99.6	Nil	0.4	N.D.	100	Nil													
3 Oct. 28 Nov. 11 1960		155	1150	284	3 6/1	21.2	368.0	79.0	115.0	24.7	36.6	22.0	32.6	21.5	99.3	Nil	0.3	0.4	99.8	Nil													
4 Dec. 17 23 1960	200	130	1250	977	2 7/1	21.0	875.0	313.0	298.0	86.4	82.5	65.0	62.2	35.8	88.3	Nil	Nil	11.7	95.5	1.2													
5 Jan. 11 14 1961	67.5	43.5	1230	562	3 7/1	22.3	206.0	136.0	106.0	94.5	74.0	87.0	68.1	66.0	76.8	Nil	0.2	22.6	99.5	Nil													
6 Feb. 10 16 1961	145	131	1250	605	2 9/1	19.8	622.0	418.0	410.0	93.9	93.6	82.2	82.1	67.2	98.2	Nil	T	1.7	92.0	7.5													
7 Mar. 26 31 1961	124	123	1190	625	1 6/1	15.5	469.0	273.0	304.0	79.2	88.6	81.7	91.3	58.2	99.1	Nil	Nil	0.9	99.03	0.22													
8 Apr. 27 28 1961	38	38	1260	515	2 1/1	14.0	108.1	74.8	77.2	86.9	89.8	83.2	85.9	69.2	94.0	2.4	3.6	Nil	95.8	2.5													
9 Jun. 3 8 1961	125	99	1255	537	2 0/1	15.4	321.5	229.0	225.0	95.6	94.0	80.7	79.3	71.4	94.8	Nil	Nil	5.2	99.0	0.95													
10	No Data Explosion and fire on 1C 4 reflux system																																
11	No Data Trial run after rebuilding pilot plant																																
12 Oct. 27 Nov. 2 1961	151.4	107.4	1250	354	4 3/1	19.2	288.4	115.7	144.7	24.5	29.2	35.9	44.8	40.1	89.2	T	0.14	10.7	94.7	5.3													
13 Nov. 11 Nov. 18 1961	76	67	1250	488	3 6/1	19.8	253.9	105.7	126.2	80.3	95.9	58.6	70.6	41.6	89.7	Nil	Nil	10.3	99.4	0.8													
14 Nov. 30 Dec. 8 1961	209	128.8	1260	392	4 3/1	19.6	390.0	259.0	268.5	81.9	84.9	67.9	70.4	66.4	92.2	Nil	Nil	7.8	96.2	3.8													
15 Jan. 3 Jan. 8 1962	125.8	103.3	1260	446	3 1/1	18.7	340.0	231.0		83.0		75.5		67.9	98.1	Nil	Nil	1.9	99.1	0.8													
16 Jan. 24 Jan. 29 1962	89	88.3	1290	531	2 5/1	17.3	319.4	206.1		58.1		70.1		64.5	98.8	Nil	Nil	1.2	100.0	Nil													

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TABLE 58

PILOT PLANT RUN SUMMARY

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Reactor Temp. (°F)	Avg. BCl_3 Feed Rate (lb./hr.)	Avg. H_2/BCl_3 Ratio (mole %)	Avg. Conversion Rate (%/Pass)	Total BHCl_2 Produced (as lbs. B_2H_6)	Total B_2H_6 Recovered (as lbs. B_2H_6)	Total HCl Recovered (as lbs. B_2H_6)	Yield Based on Make-up BCl_3		Yield Based on Make-up H_2		DIBORANE PRODUCT ANALYSES				HCl PRODUCT ANALYSES				REMARKS
							% B_2H_6	% HCl	% B_2H_6	% HCl	% B_2H_6	Mole % B_2H_6	Mole % BCl_3	Mole % BHCl_2	Mole % HCl	Mole % HCl	Mole % BCl_3	Mole % BHCl_2	
955	3 0/1	20.0		7 51 lb/hr	52.4 lb/hr	100	100	100	100	100	100				100				
630	3 3/1	7.4	44.0	0		0	0	0	0	0									Inability to establish reflux on IC-4 plus other mechanical difficulties forced termination of run
660	2 2/1	18.3	348.0	13.5	27.0	12.4	25.7	6.8	14.1	3.9	99.6	Nil	0.4	N.D.	100	Nil	Nil	Nil	Unable to take off diborane product which led to high B_2H_6 recycle
284	3 6/1	21.2	368.0	79.0	115.0	24.7	36.6	22.0	32.6	21.5	99.3	Nil	0.3	0.4	99.8	Nil	Nil	0.2	Continued difficulty in diborane take off. High pressure drop through reactor indicated plugging
977	2 7/1	21.0	875.0	313.0	298.0	86.4	82.5	65.0	62.2	35.8	88.3	Nil	Nil	11.7	95.5	1.2	0.7	2.6	Plant steam pressure low
562	3 7/1	22.3	206.0	136.0	106.0	94.5	74.0	87.0	68.1	66.0	76.8	Nil	0.2	22.6	99.5	Nil	0.05	0.5	Plant steam pressure low
605	2 9/1	19.8	622.0	418.0	410.0	93.9	93.6	82.2	82.1	67.2	98.2	Nil	Tr	1.7	92.0	7.5	0.5	Nil	Recurring plug in hydrogen make up line. Some minor upsets in refrigeration system
625	1 6/1	15.5	469.0	273.0	304.0	79.2	88.6	81.7	91.3	58.2	99.1	Nil	Nil	0.9	99.03	0.22	0.12	0.63	Low natural gas pressure resulted in low reaction temperature and low conversions. IG-3 seal leaked
515	2 1/1	14.0	108.1	74.8	77.2	86.9	89.8	83.2	85.9	69.2	94.0	2.4	3.6	Nil	95.8	2.5	0.6	1.1	Refrigeration system failure forced premature termination of run
537	2 0/1	15.4	321.5	229.0	225.0	95.6	94.0	80.7	79.3	71.4	94.8	Nil	Nil	5.2	99.0	0.95	0.05	Nil	Both hydrogen recycle compressors failed. Also refrigeration difficulties continued.
4 reflux system																			
pilot plant																			
354	4 3/1	19.2	288.4	115.7	144.7	24.5	29.2	35.9	44.8	40.1	89.2	Tr	0.14	10.7	94.7	5.3	Nil	Nil	Many mechanical difficulties
488	3 6/1	19.8	253.9	105.7	126.2	80.3	95.9	58.6	70.6	41.6	89.7	Nil	Nil	10.3	99.4	0.8	Nil	Nil	
392	4 3/1	19.6	390.0	259.0	268.5	81.9	84.9	67.9	70.4	66.4	92.2	Nil	Nil	7.8	96.2	3.8	Nil	Nil	
446	3 1/1	18.7	340.0	231.0		83.0		75.5		67.9	98.1	Nil	Nil	1.9	99.1	0.8	0.1	Nil	100 refrigeration failed
531	2 5/1	17.3	319.4	206.1		58.1		70.1		64.5	98.8	Nil	Nil	1.2	100.0	Nil	Nil	Nil	100 refrigeration failed

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3. Per pass conversions of BCl_3 to BHCl_2 in the hydrogenation reactor achieved the design figure of 20 per cent (Ref. Runs 3, 4, 5) at the design flow rate (Run 4). Conversions fluctuated as expected under varying conditions of temperature and H_2 to BCl_3 ratio. Within the limits of analytical accuracy (sampling and analysis of reactor effluent was quite difficult and required a statistical approach for meaningful results), no loss in effectiveness of the catalytic reactor was noted in the period of pilot plant operation.
4. Yields of product and by-product, based on BCl_3 consumed, were in the order of 93 to 95 per cent (Ref. Runs 5, 6, 9). Yields based on H_2 were somewhat lower, probably due to physical losses.
5. The feed rates to the reactor were usually kept at about 60 per cent design. A lower rate was necessary because product purity suffered greatly at high flow rates. This problem was the result of an unexpectedly low capacity of the absorption section (1C-1 and 1C-2) for separating HCl and BHCl_2 and will be discussed later in the report.

In this complex plant, it was necessary that literally hundreds of individual equipment items function effectively for the unit as a whole to give its best performance. Since no spare equipment had been provided because of the experimental nature of the operation, results were sometimes obscured by the occurrence of normal equipment malfunctions. The sixteen runs did provide ample data to permit evaluation of the process and gave an adequate supply of B_2H_6 for operation of the pyrolysis unit (Step II).

Typical curves for the cumulative production of B_2H_6 , HCl and BHCl_2 are shown in Figures 51 and 52. The top curve in both figures shows the B_2H_6 equivalent in pounds of the boron-hydrogen bonding leaving the reactor as BHCl_2 . The curve labeled B_2H_6 shows the pounds of B_2H_6 actually recovered while the HCl curve gives the B_2H_6 equivalents in the slopes of the two sets of curves is indicative of the improvements achieved in the performance and operation of the pilot plant in the period between Run 3 and Run 9.

The difference between the BHCl_2 curve and the B_2H_6 curve is a measure of the boron-hydrogen bondings not recovered during the run. There are four possible means that this apparent loss of boron-hydrogen bonds can take place:

1. Physical loss or venting of either BHCl_2 or B_2H_6 .
2. Back reaction, i.e.,



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3. Polymerization of BHCl_2 or B_2H_6 to form solids.
4. Build-up of inventory in the system of boron-hydrogen bonded compounds which were not recoverable and lost at run termination due to back reaction.

The more important of these were (1) and (2) which will be discussed under Equipment Performance.

IV. Calculations

The conversions and yields, as referred to in this report, are expressed by:

$$\% \text{ Conversion} = \frac{\text{Moles BHCl}_2 \text{ produced per pass}}{\text{Moles BCl}_3 \text{ fed to reactor per pass}} \times 100$$

$$\% \text{ Yield (B}_2\text{H}_6\text{) based on make-up BCl}_3 = \frac{\text{Moles B}_2\text{H}_6 \text{ recovered}}{\text{Equiv. moles BCl}_3 \text{ consumed}} \times 100$$

$$\% \text{ Yield (HCl) based on make-up BCl}_3 = \frac{\text{Moles HCl (as B}_2\text{H}_6\text{)}}{\text{Equiv. moles BCl}_3 \text{ consumed}} \times 100$$

The actual procedures used to calculate the results of the Step I runs are given in detail in Appendix L. A complete sample calculation is also shown in Appendix L.

For calculation purposes, the starting time of each run was taken as the time when the BCl_3 feed to the reactor was first started, and the end of the run was taken as the time when the BCl_3 feed to the reactor was shut off. In reality, all equipment was started up and in operation for some time before the process temperatures, flows, etc. reached steady state conditions and the run could begin. Usually eight to ten hours were required to achieve satisfactory conditions so that the BCl_3 feed to the reactor could be started. By the same token, the pilot plant normally remained in operation for several hours after the BCl_3 flow to the reactor ceased. This enabled the reactor to cool down slowly and permitted the recovery of most of the B_2H_6 and HCl left in the system at shutdown.

During an actual run, process or mechanical operating difficulties sometimes resulted in the shut off of the BCl_3 feed to the reactor. This did not necessarily end the run. If the difficulty could be corrected in a reasonable time and the BCl_3 flow resumed, the run would be continued. For this reason, two operating times are reported for each run, the first being the total time from the start to final shutdown of the run, and the second, the actual length of time BCl_3 was fed to the reactor. In general, the difference between the two is an indication of the number or seriousness of mechanical problems encountered during the run.

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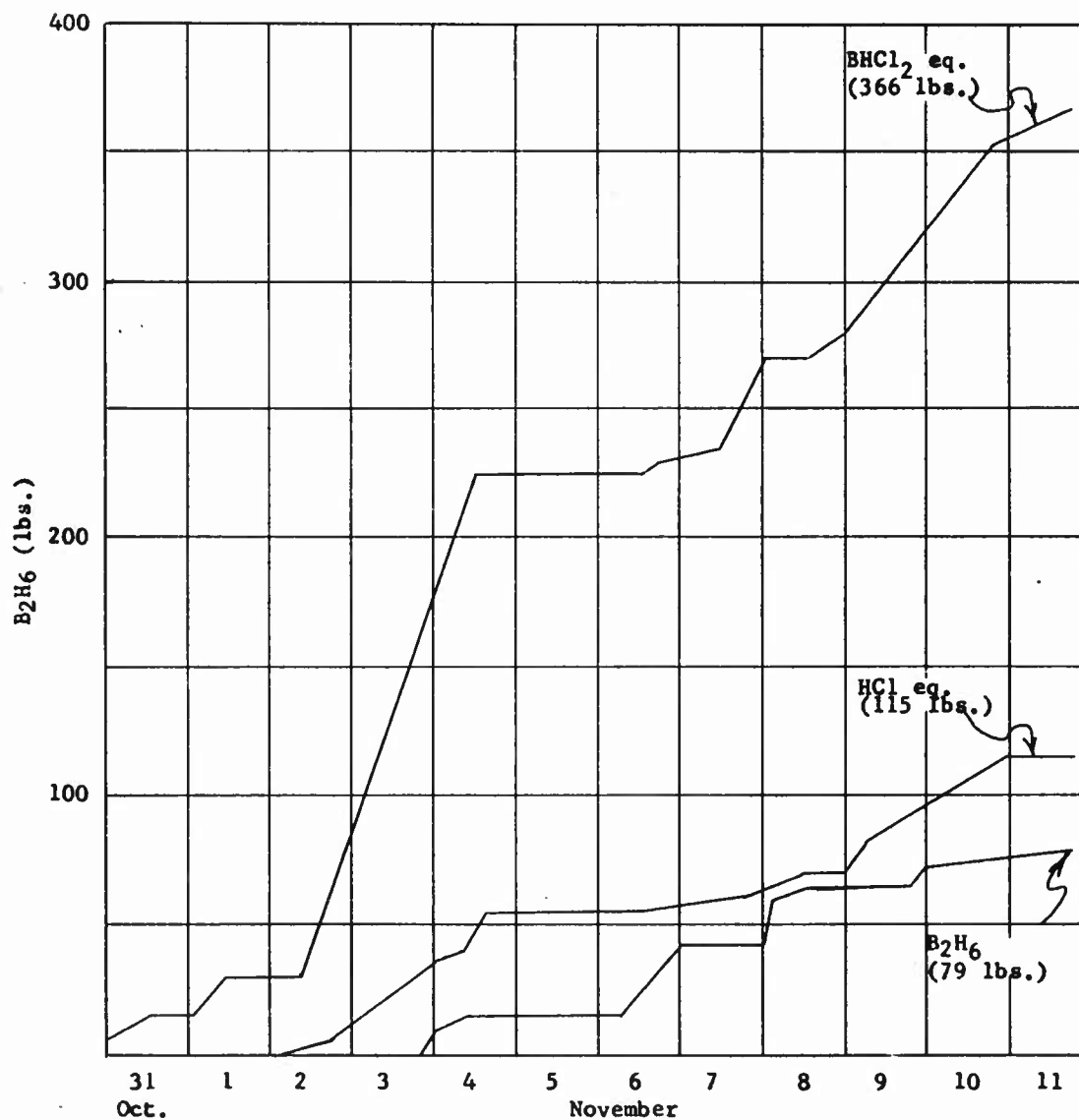


Figure 51. Cumulative Production Data - Run 3

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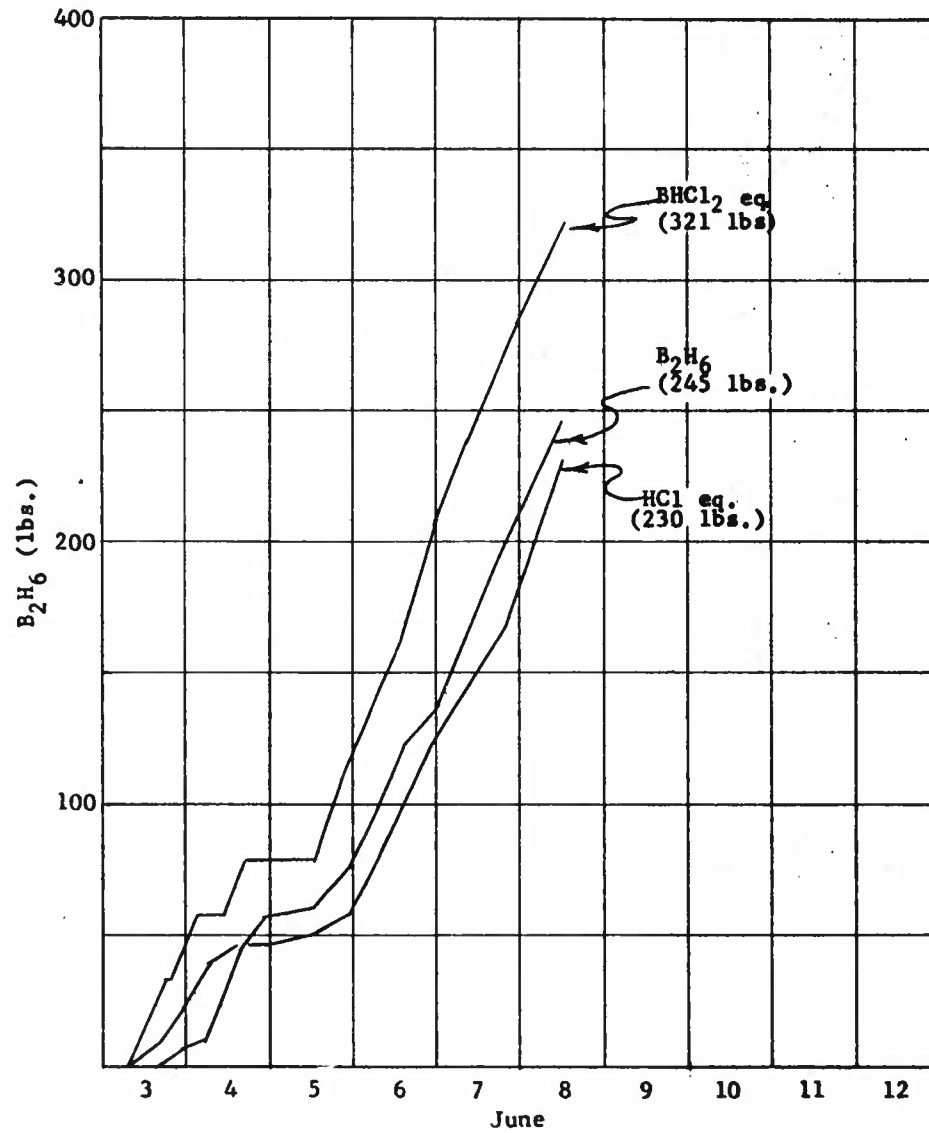


Figure 52. Cumulative Production Data - Run 9

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V. Equipment Performance

In general, the pilot plant performed and was operated in the manner described in the preceding part of this report (Pilot Plant Design). Only two changes were made in the flow paths shown in Figure 45:

1. After Run 2, the discharge of the make-up hydrogen compressor (1K-2) which also handles the overhead gas from the B_2H_6 absorber (1C-8), was rerouted to the bottom of the primary absorber (1C-1) where it supplemented the stripping gas. This change was desirable to prevent B_2H_6 , which sometimes broke through the top of the absorber under upset conditions, from being fed to the reactor (1F-1, 1F-2) by way of the H_2 recycle compressor (1K-1). The high temperatures of the reactor section would of course cause pyrolysis of the B_2H_6 with consequent solids formation and plugging of the reactor.
2. After Run 3, the bottoms liquor from the B_2H_6 absorber (1C-8) was rerouted to go to the reflux accumulator of the prefractionator (1C-3) rather than to the feed of that column. This stream was rich in dissolved B_2H_6 and it was considered best to shorten the recycle path traced by this B_2H_6 , thereby minimizing possible losses through back reaction or polymerization.

Other important changes were made to improve mechanical performance of certain pieces of equipment and will be discussed as the various sections of the diborane plant are reviewed.

Detailed operating instructions are included in Appendix J.

A. Reactor Section

The hydrogenation reactor (1F-1, 1F-2) was in operation for over 1300 hours with no evidence of a decrease in the activity of the silver screen catalyst, nor was any chemical attack of the silver lining used in the reactor and feed-effluent exchanger (1E-1) apparent. These were examined visually prior to a clean-out after Run 3, but were not opened up again.

Analysis of samples of the reactor effluent stream after it had passed through the quench exchanger (1E-1) and the BCl_3 vaporizer (1E-2), indicated that these units were effective in "freezing" the favorable equilibrium existing at the reactor temperature. The back reaction:



received detailed consideration during the bench scale and design phases, as previously reported, and 1E-1 was specifically constructed to cool the

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reactor effluent quickly to avoid this effect. Since design conversion rates were obtained, it must be concluded the reactor section, illustrated schematically in Figure 53, met all expectations.

It became apparent early in Run 2 that the design reactor temperature, 1290°F., could not be achieved. Struthers-Wells Corporation, designer and supplier of the furnace, was contacted on this matter and larger gas burners for the reactor furnace were supplied. The replacement burners, installed after Run 3, proved to be adequate in subsequent runs. At the same time, it was noted that the refractory surrounding the burner ports had deteriorated in several places. A different type of high temperature castable refractory was used to repair the defective areas, and in fact to provide a new combustion tube for each of the 36 burners. No further attention was required by the refractory during the remainder of pilot plant operations.

A similar problem arose with respect to the thermocouples installed to measure the outside wall temperature of the reactor. One by one, these became inoperative in the first runs; therefore, they were removed and returned to the supplier for repair after Run 3. It developed that their sheath tips had originally been silver soldered and could not withstand the normal furnace temperatures. In addition, deterioration and shifting of the refractory had caused some mechanical damage. When repaired, the thermocouples performed satisfactorily although some failures started developing in the last few runs. Apparently a thermocouple construction better tailored to this environment is needed. The thermocouples within the reactor itself (TRC-47, 48) performed very well.

The early runs also indicated the need for protecting the reactor from solids accumulation. When the pressure drop through the reactor section (1E-1, 1F-1,2) became excessive in Run 3, these units were opened for examination and then washed out. Approximately one pound of solids was found in the reactor. Most of this undoubtedly resulted from the recycle of B_2H_6 to the reactor as previously noted; further trouble from this source was prevented by the piping change. Additional protection against solids deposition was provided by the installation of a porous metal filter in the reactor feed line between the two exchangers (1E-1, 2). Although the liquid BCl_3 and H_2 feeds were filtered separately, it was possible that some B_2O_3 , in the form of soluble triboronoxychloride ($B_3O_3Cl_3$) had been passing through the BCl_3 polishing filter (1V-1) but would be removed in this new filter. These changes were effective in preventing any further problems with reactor plugging.

B. Separation Section

The most serious process problem encountered in the operation of the pilot plant proved to be the separation of $BHCl_2$ and HCl in the primary absorber (1C-1). Any $BHCl_2$ going overhead was absorbed in the secondary absorber and eventually wound up in the HCl fractionator (1C-5). Here

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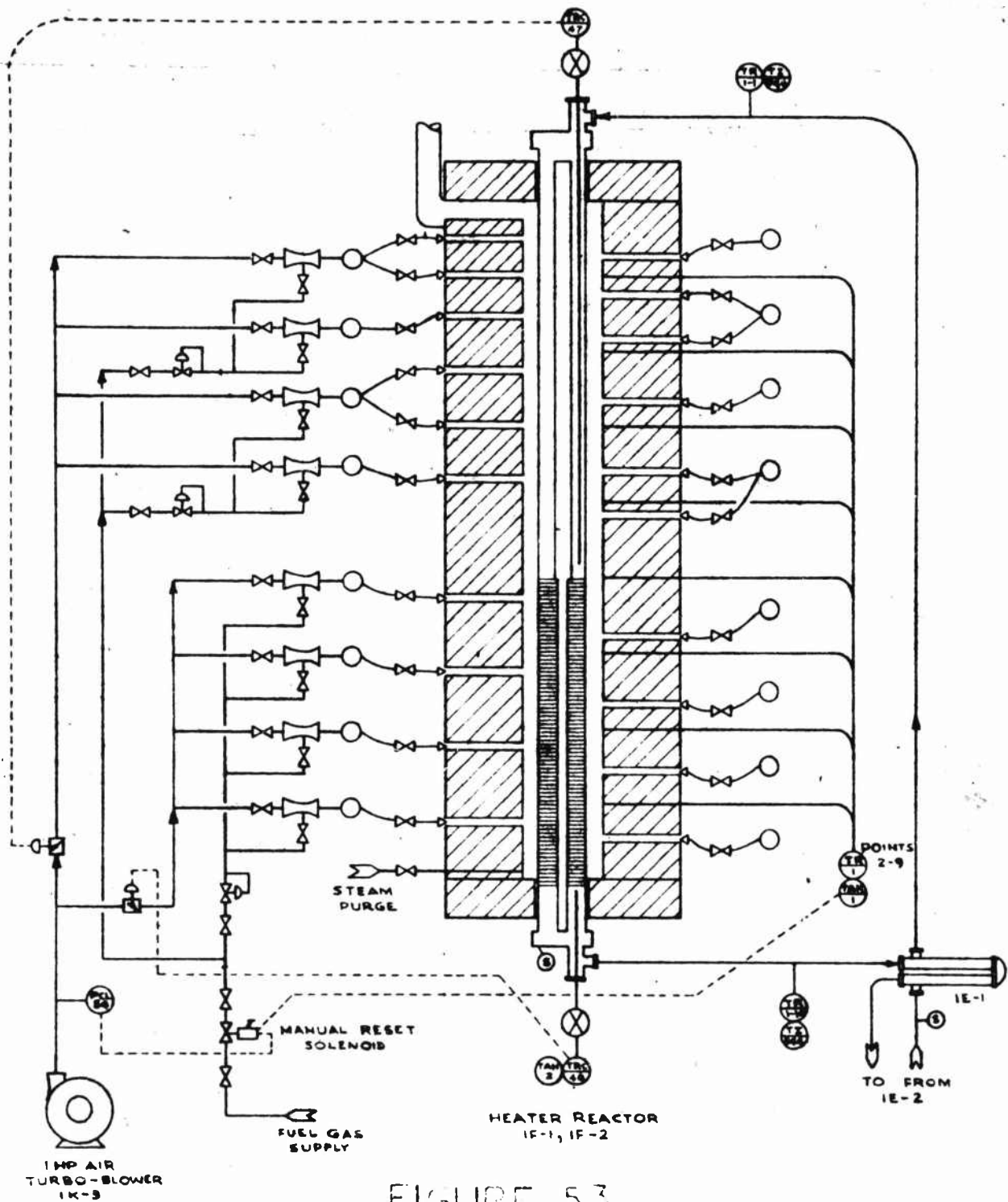


FIGURE 53

AFN, Inc.
LOS ANGELES, CALIFORNIA

DATE 6-2-60	DRAWN N. REGAN	STEP I REACTOR SECTION	DRAWING NO.
SCALE NONE	APPROVED		PFS-260

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some of the BHCl_2 disproportionated to form B_2H_6 which went overhead and contaminated the HCl by-product. The remainder either back reacted with HCl to form BCl_3 or left the fractionator in the bottoms liquid recycling to the reactor (1F-1, 1F-2).

At the same time, any HCl leaving the primary absorber in the bottoms liquor was fed to the DCB prefractionator (1C-3). A small portion of this HCl , which has a vapor pressure close to B_2H_6 and was therefore not separable in the pilot plant distillation columns, passed through the prefractionator (1C-3) and the disproportionator (1C-4) to become a major contaminant in the product. Again, the back reaction between HCl and BHCl_2 , forming the primary reactants H_2 and BCl_3 , disposed of the major portion of the HCl in the underflow from the primary absorber (1C-1).

Back reactions were found to have a very favorable influence on pilot plant results. It is apparent from the above discussion that the purity of both the product, B_2H_6 , and the by-product, HCl , was materially improved by the back reactions taking place in the distillation columns. The laboratory development program had shown that HCl back reacts not only with BHCl_2 but also with B_2H_6 :



Undoubtedly this reaction contributed appreciably to the built-in purification process. While it was suspected that this process continued to a limited degree in the refrigerated storage tanks (1C-7A,B and 9), the data obtained were not consistent enough to prove it conclusively due to the problems inherent in obtaining a very small but representative sample from a large, static tank of liquid.

While these back reactions in the distillation columns were beneficial, a similar reaction in the primary absorber (1C-1) would result in a loss of BHCl_2 , thus reducing the plant's productivity. However, material balance calculations around the primary absorber, based on analytical and flow data, failed to show any such loss. Apparently the lower temperature of the column and short liquor hold-up time effectively prevented appreciable back reaction.

As indicated in Table 58 (Run Summary Data), HCl contamination of the product first occurred in Run 4. In the first three runs, reactor throughput and conversion had been low due to the limited capacity of the furnace burners and the separation system was adequate. In Run 4, design flow rates and conversion were achieved with the result that the primary absorber (1C-1) did not perform a satisfactory separation. This condition was not detected during the run because (1) the absorber bottoms were not analyzed for HCl since no analytical methods were available to detect a small amount of HCl in liquid BCl_3 , and (2) the infrared analysis used to monitor the product B_2H_6 was also insensitive to HCl . It was not until a more detailed analysis of the product collected in the tank was

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performed at the end of Run 4 that the gross product contamination was discovered. In the remaining runs, product samples were periodically analyzed for HCl by hydrolysis and absorber performance inferred by the results.

In the runs immediately following, reactor feed rates were reduced to enable the absorber section to make a better BHCl_2 -HCl separation with some degree of success. Performance of the primary absorber (1C-1) was found to be directly related to reactor feed rate as shown in Figure 54.

Because of the integrated nature of the pilot plant, the efficiency of separation accomplished by the primary absorber was dependent upon the performance of other equipment items. For example, the overhead gas from the secondary absorber (1C-2) had to be free of HCl or the stripping gas to the primary absorber (1C-1) could not possibly remove the HCl there. Similarly, the bottoms of the HCl fractionator (1C-5) had to contain no HCl if the absorbent to the secondary absorber (1C-2) were to completely remove HCl from its overhead. Again, the HCl content of the overhead gas from the secondary absorber could not be determined with precision because of the BCl_3 also present. However, the continuous H_2 analyzer monitoring this stream did indicate changes in H_2 purity and provided a means of evaluating changes in operating conditions. High absorbent flow rate, low absorbent temperature, and smooth operation of the HCl fractionator (1C-5) were conducive to highest H_2 purity. By following these conditions carefully and keeping the reactor feed rate at about 60 per cent of design, B_2H_6 product purities of 94 to 99 per cent were obtained in Runs 6 to 9.

While these operational investigations were proceeding, the problem was examined from an engineering standpoint. The effect of an incomplete HCl- BHCl_2 separation on product and by-product purity, assuming no subsequent back reaction, was determined. Results are shown in Figures 55 and 56. In addition, the effects of HCl contamination of the stripping gas on B_2H_6 purity were calculated (Figure 57). The amount of HCl to be expected in this stripping gas (Figure 58) as the consequence of a given percentage of HCl in the absorbent (1C-5 bottoms) was also calculated. These calculations all indicate that a very complete separation was required in all columns if the desired purity were to be obtained.

The next step was to ascertain what could be done to improve the plant's performance. Bechtel Corporation engineers reviewed their original design calculations and concluded that gas underloading of both absorbers (1C-1 and 1C-2) was the probable cause for their inability to perform as expected, and that repacking of these columns with 1/4 inch Raschig rings would remedy the situation without causing excessive drop. Accordingly, the original Intalox saddles were removed after Run 9 and replaced with 1/4 inch metal Raschig rings dry dumped into place and settled by tapping the sides of the columns. At the same time, an additional -20°F. exchanger (1F-23) was installed in the absorbent line to the secondary absorber to relieve part of the load on the -50 exchanger (1E-13) and insure the coldest possible absorbent.

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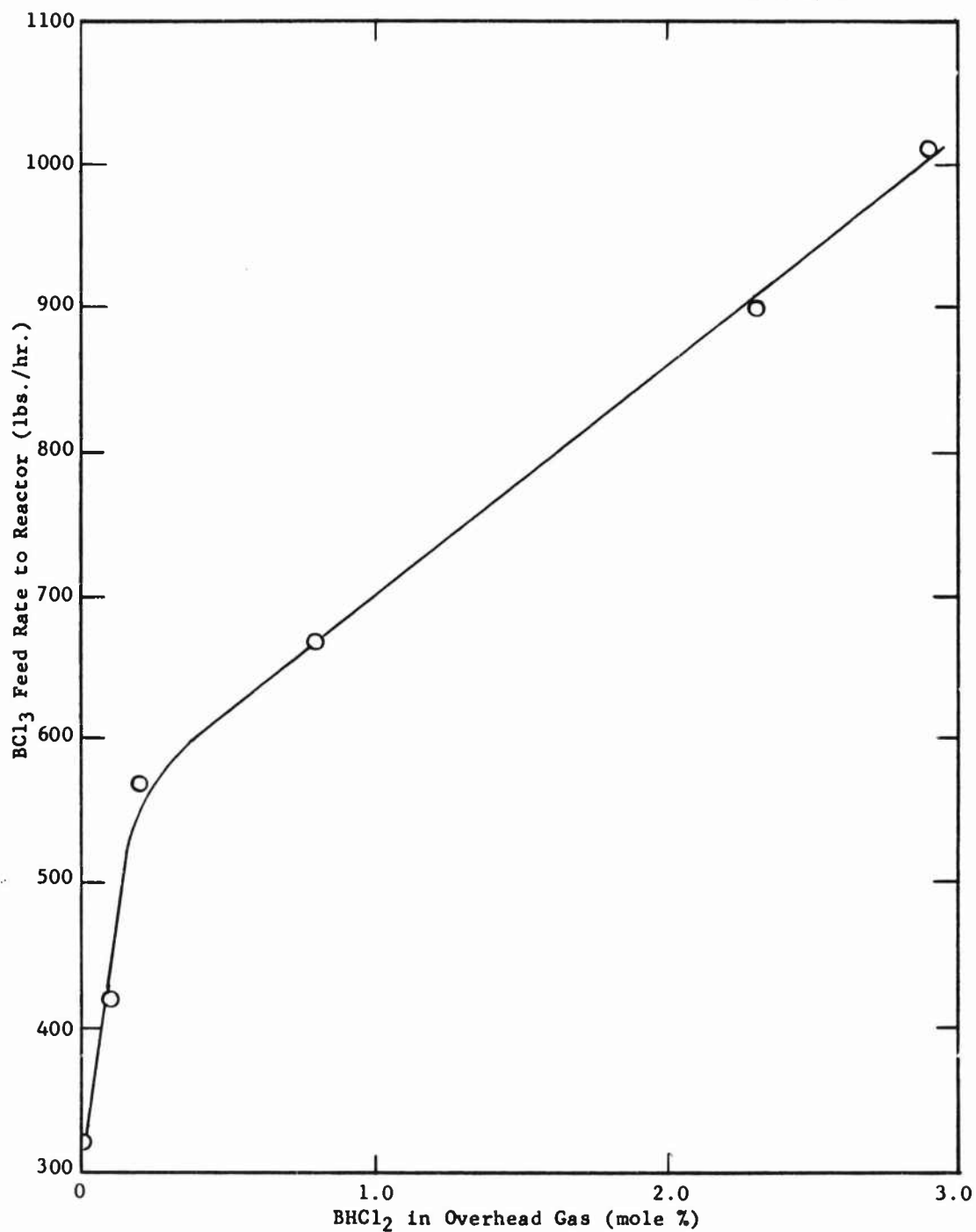


Figure 54. Performance of Primary Absorber (1C-1) as Related to BCl₃ Feed Rate to Reactor (1F-1,2).
Data from Runs 4, 5 and 6.

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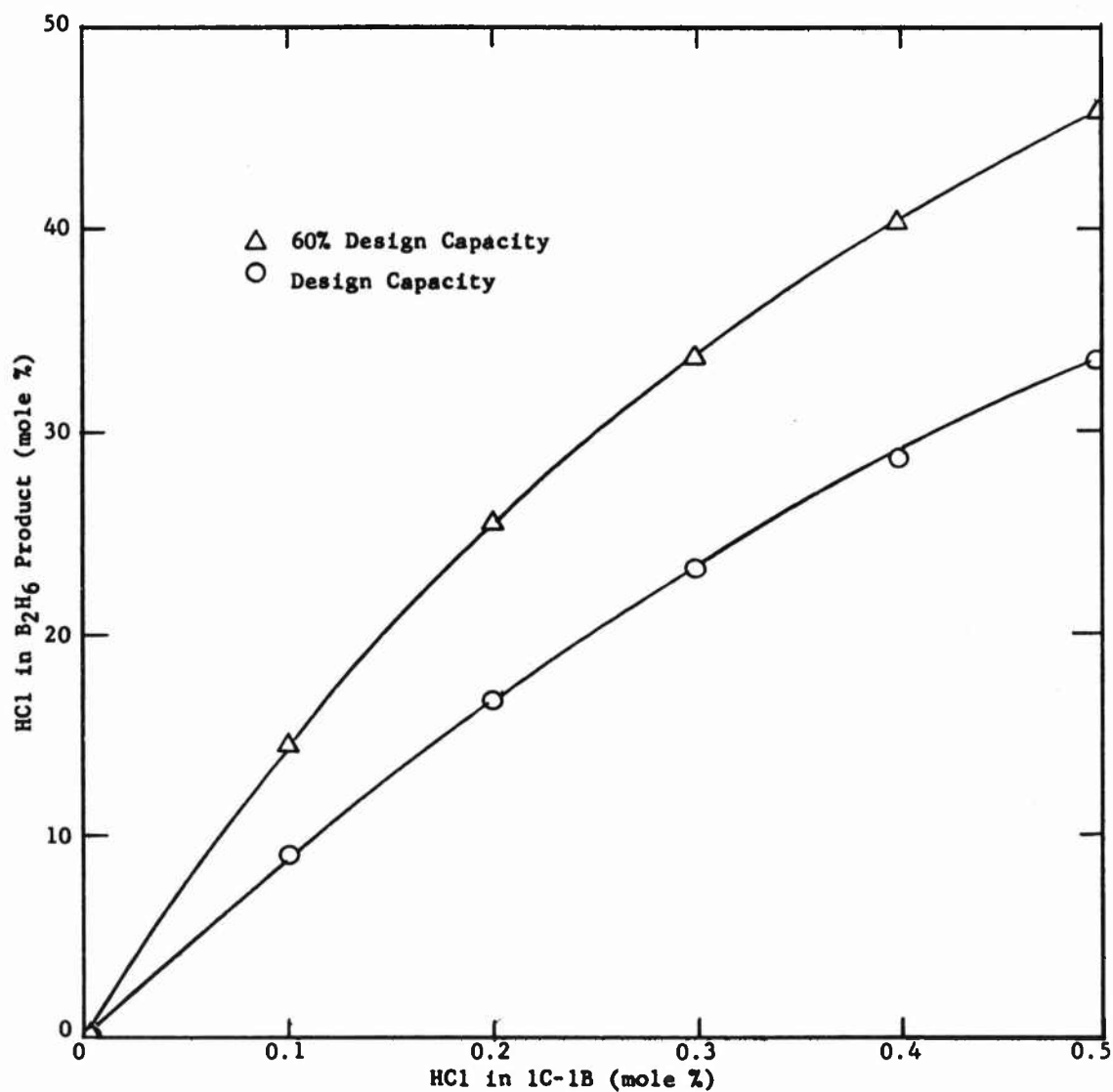


Figure 55. Effect of Primary Absorber Functioning on Product Purity

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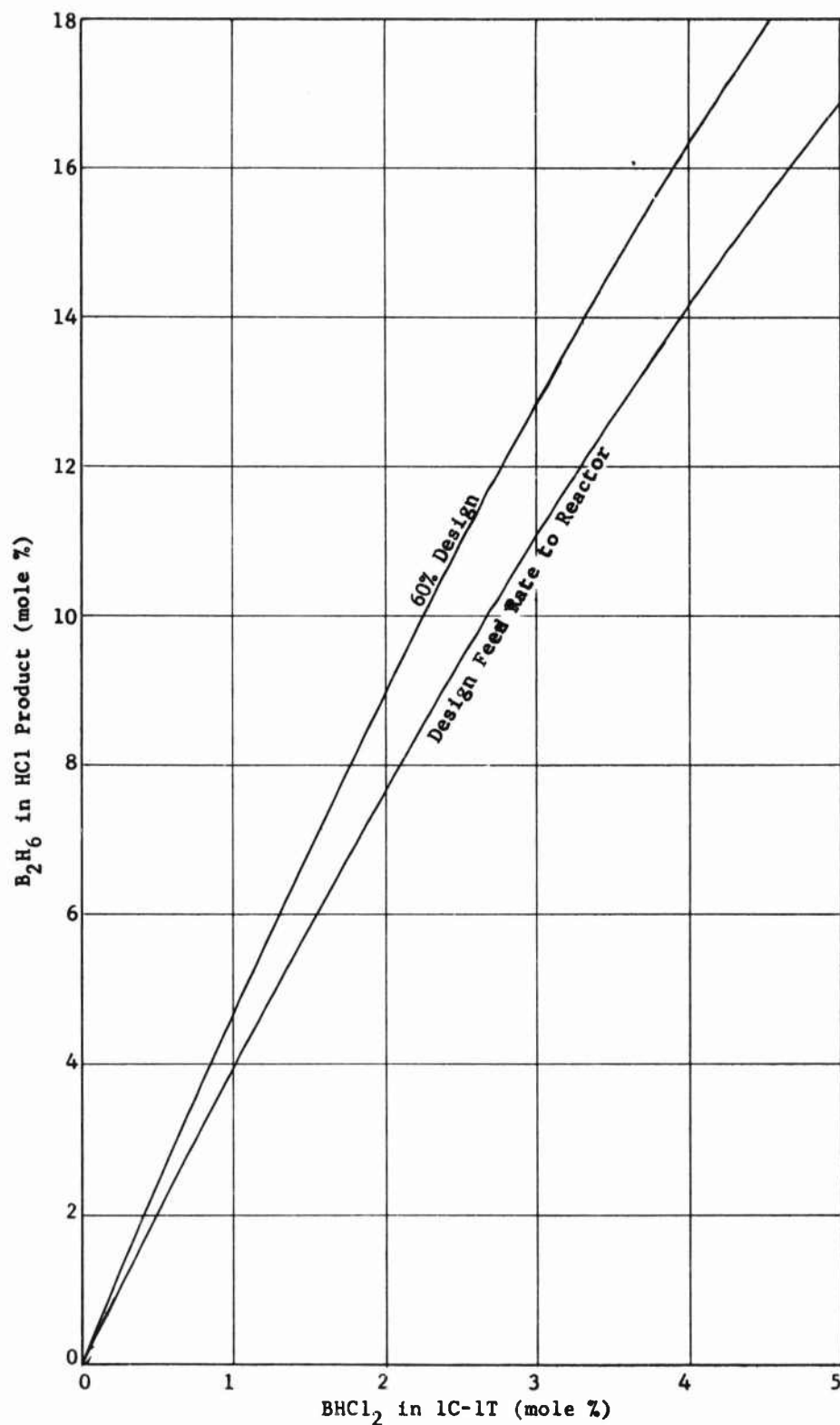


Figure 56. HCl Purity - Effect of Dichloroborane in Primary Absorber Overhead

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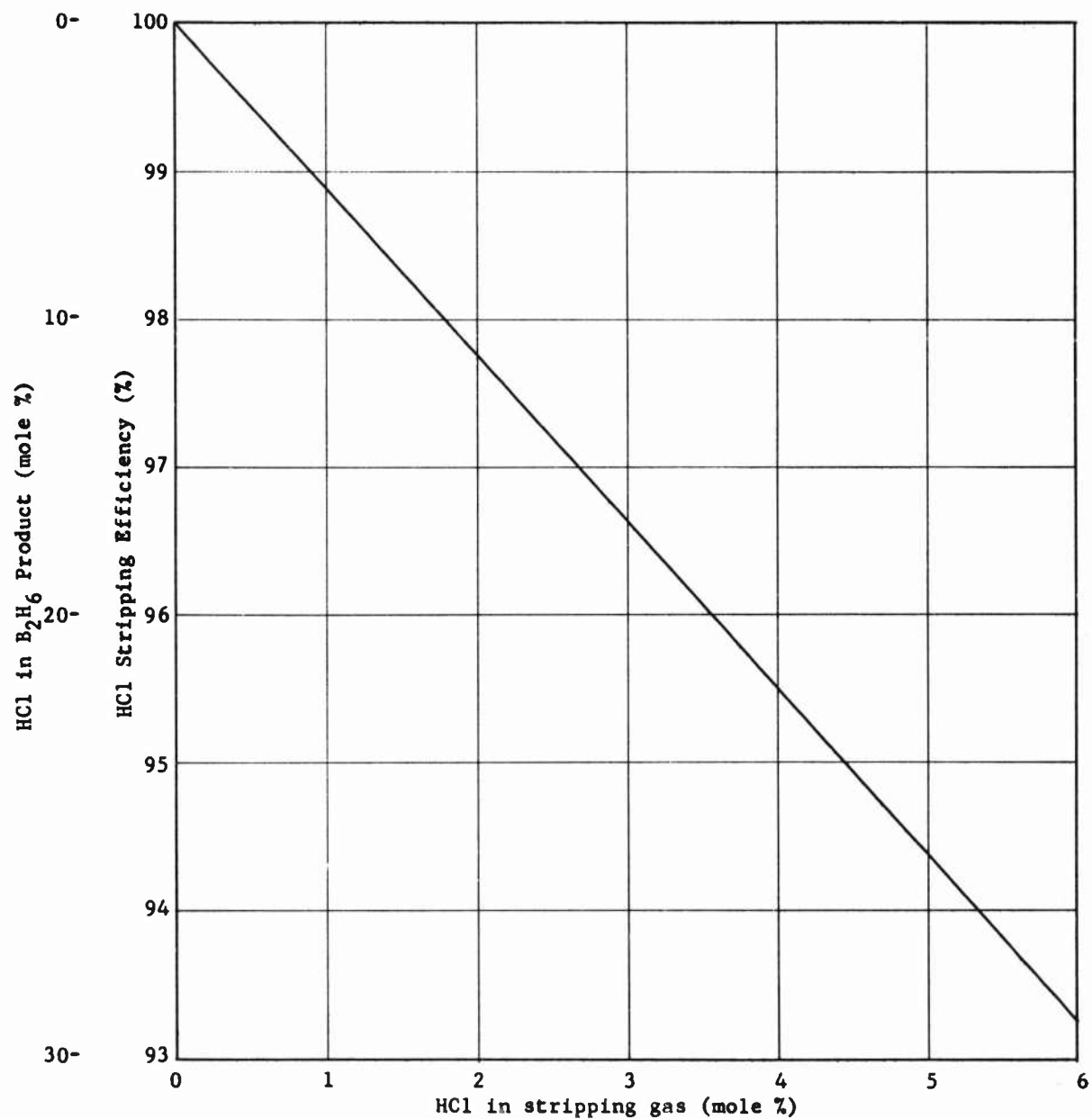


Figure 57. HCl Stripping Efficiency in 1C-1 as a Function of
HCl in Stripping Gas (Base 100% at 0% HCl
in Stripping Gas)

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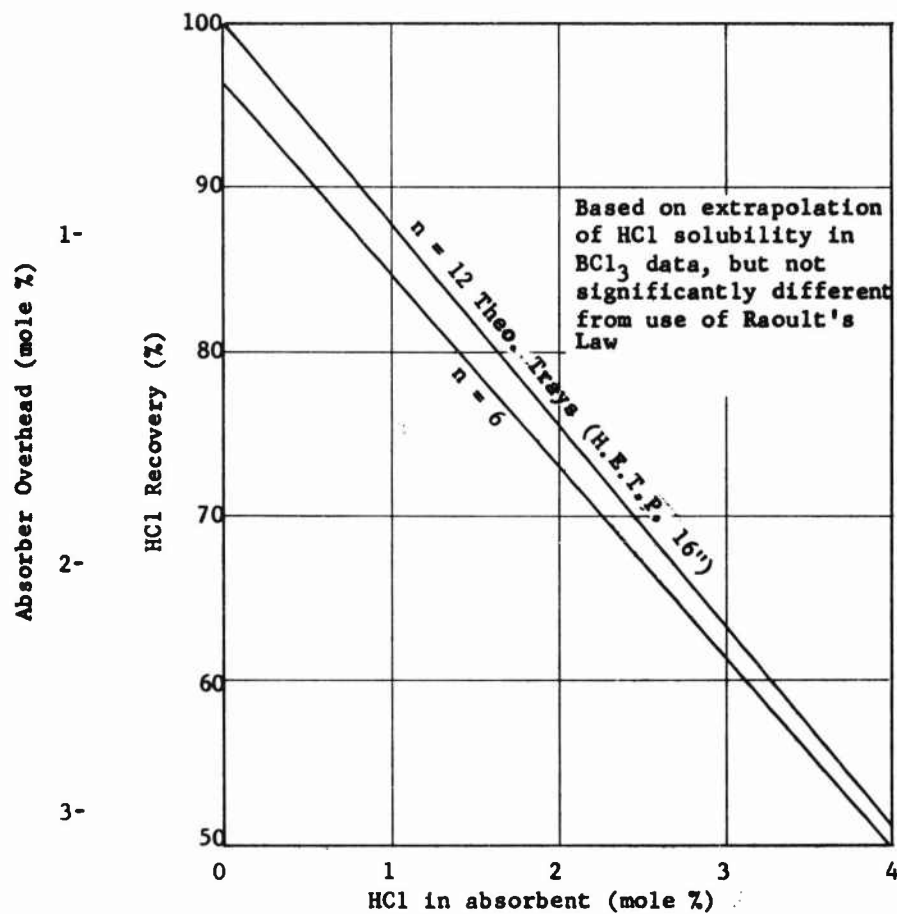


Figure 58. Effect of Impure Absorbent on HCl Recovery - Secondary Absorber Operation

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Upon starting Run 10, it was found that flooding of both absorbers occurred at approximately 60 per cent of design flow rates. This result contrasted with Bechtel Corporation's calculations, and it became necessary to determine the reason for it. Partially plugged packing support plates could have caused the problem.

Additional tests were performed on pilot plant equipment and the packing calculations were reviewed with the conclusions that (1) the columns did give the proper physical response, and (2) U. S. Stoneware's "Generalized Pressure Drop Correction", used by Bechtel in their calculations, was inadequate for the circumstances encountered. Probably the correlation was unsatisfactory in this case because the gas and liquid involved, i.e., H_2 and BCl_3 , respectively, represent extremes in density as compared to such materials as ammonia and water, which typically provided most of the basic data for the correlation. Moreover, the packing factor, an important element in making the pressure drop calculations, was given by U. S. Stoneware for 1/4 inch metal Raschig rings as an extrapolated value and was therefore unsuitable. Other correlation methods applied to this problem indicated flooding at design rates for the two absorption columns. Figure 59 illustrates the results of the "Generalized Pressure Drop Correlation" method, while Figure 60 shows the results of another correlation. (12)

In view of this more intensive study, both the primary and secondary absorbers (1C-1 and 1C-2) were repacked with 1/2 inch Intalox saddles, but the latter was returned to its "as built" condition. Since the opportunity presented itself, the 1/2 inch Intalox saddles in the B_2H_6 absorber (1C-8) were also replaced with 1/4 inch metal Raschig rings after first calculating pressure drop by various methods. Although this column had performed well, the change made it even more efficient.

After this second repacking was completed prior to Run 11, some improvement in the column efficiencies was found. Dichloroborane in the primary absorber overhead was reduced to a minimum and no $BHCl_2$ or B_2H_6 was found in the by-product HCl from these runs. However, the stripping of HCl from the primary absorber bottom liquor was still not complete and HCl was found in the B_2H_6 . Investigation revealed that the absorber bottom temperature was only 25 to 30°F. Design temperature was 70°F. Refrigeration modifications during the July and August shutdown period had resulted in a substantially reduced temperature of the absorbent to the secondary absorber and thereby reduced the BCl_3 content of the recycle gas stream used as stripping gas for the primary absorber. Boron trichloride was evaporated by this stripping gas in the stripping section of the absorber, cooling the remaining liquid below design.

Since the solubility of anhydrous HCl in BCl_3 varies inversely with temperature, this condition contributed to the appreciable HCl contamination of the product B_2H_6 during Runs 12, 13 and 14. Therefore, prior to Run 15, the recycle H_2 cooler (1E-6) was changed to permit heating of the stripping gas to 270 to 280°F. By this means, the primary absorber bottoms

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temperature was increased to approximately 60°F. during the last two Step I runs, and the HCl concentration in the B_2H_6 was reduced to less than 2.0 per cent.

The pilot plant operation uncovered no peculiarities of the HCl- BCl_3 systems which would rule out the efficient separation of HCl and $BHCl_2$ by absorption. More efficient packing, if flooding could be avoided, or longer columns would undoubtedly make operation at design conditions possible.

C. Distillation Section

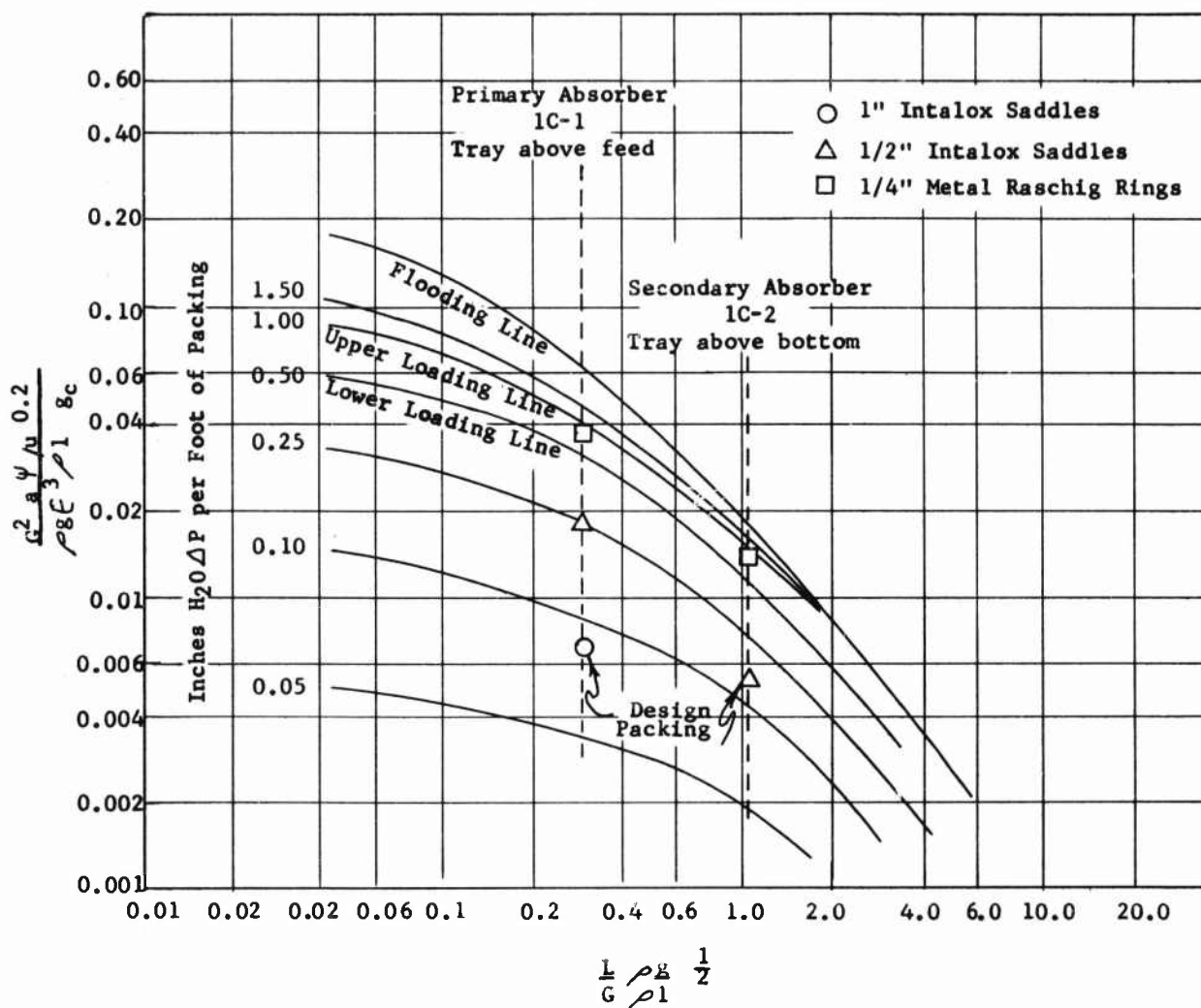
1. DCB Prefractionator (1C-3)

The DCB prefractionator (1C-3) was designed to separate $BHCl_2$ from the absorbent BCl_3 by distillation, sending $BHCl_2$, B_2H_6 and some BCl_3 overhead to the disproportionator (1C-4) while producing pure BCl_3 as a bottoms product for recycle as absorbent to the primary absorber. Performance of the prefractionator was adequate. The column proved capable of producing a relatively pure bottoms product at design ratios. During most of the runs, the $BHCl_2$ content of the absorbent to the primary absorber was usually nil although occasional values were as high as 0.3 mole per cent.

The column reflux, however, was not steady during normal operation, fluctuating as much as 1000 per cent. This condition caused substantial variations in the bottoms level, frequently threatening to starve the bottoms pump, as well as the feed rate to the disproportionator (1C-4). It is believed that the sporadic disproportionation of $BHCl_2$ to B_2H_6 was the basic cause since the operation was always very steady at run start-up when there was no $BHCl_2$ in the system. Since the disproportionation reaction produces a total of 5 moles of B_2H_6 and BCl_3 for the 6 moles of $BHCl_2$ reacted, rapid disproportionation could cause a pressure change with a resultant variation in reflux rate. The consequences of this phenomenon were minimized by careful control of the column without detriment to the over-all plant operation. Addition of a larger surge volume to the vapor space of the reflux accumulator to reduce pressure surging would probably eliminate most of the fluctuations.

During the first few runs, the steam pressure on the prefractionator reboiler (1E-15), required to maintain the desired boil-up, gradually increased. This was correctly interpreted as resulting from fouling of the reboiler surfaces with solids, as examination of the reboiler after Run 3 disclosed. The process side of the exchanger was washed and dried, and a filter was installed on the discharge of the bottoms pump (1G-3). This measure was effective in controlling solids build-up thereafter. Since there normally was very little liquid outflow from the primary absorber (1C-1)-prefractionator (1C-3) loop, solids naturally tended to accumulate there. Thus when the new filter started removing them, solids were reduced to a generally low level throughout the plant.

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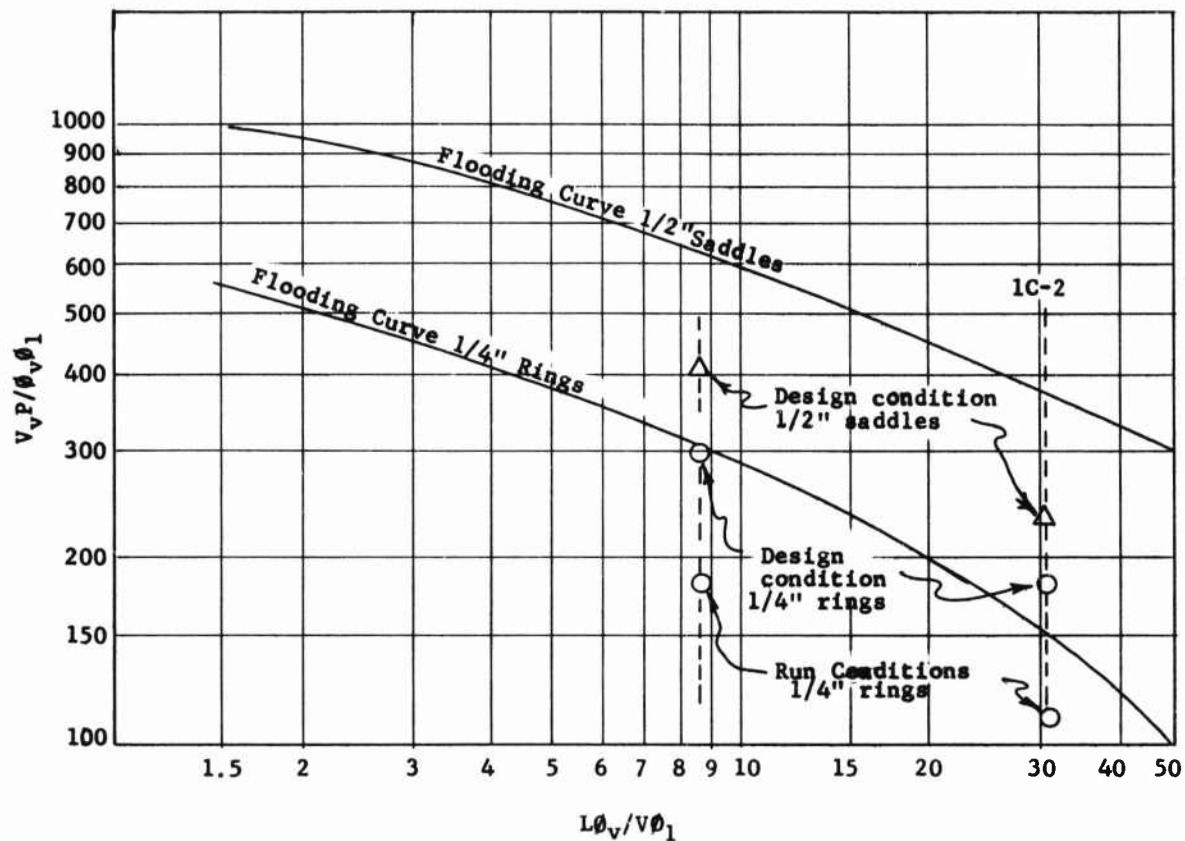
- L = Liquid Rate, lbs./sec., sq. ft.
 G = Gas Rate, lbs./sec., sq. ft.
 ρ_l = Liquid Density, lbs./cu. ft.
 $\rho_a/83$ = Packing Factor F
 μ = Viscosity of Liquid, Centipoise
 ψ = Ratio, $\frac{\text{Density of Water}}{\text{Density of Liquid}}$
 g_c = Gravitational Conversion Factor = 32.2

Figure 59. Diborane Process. Application of U. S. Stoneware's "Generalized Pressure Drop Correlation" to Primary and Secondary Absorbers (1C-1, 1C-2). Design Packing vs. 1/4" Metal Raschig Rings at Design Flow Rates.

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- L = Liquid rate (lbs./hr.-sq.ft.)
- V = Vapor rate (lbs./hr.-sq.ft.)
- δ_l = Liquid density factor (density in lbs./cu.ft./62.3)^{0.5}
- δ_v = Vapor density factor (density in lbs./cu.ft./0.75)^{0.5}
- V = Kinematic viscosity (centistokes)
- P = Empirical exponent (0.12 for 1/2" saddles, 0.33 for 1/4" rings)

Figure 60. Diborane Process. Results of Flooding Calculations for Primary and Secondary Absorbers (1C-1, 1C-2) at Design and Run 10 Conditions

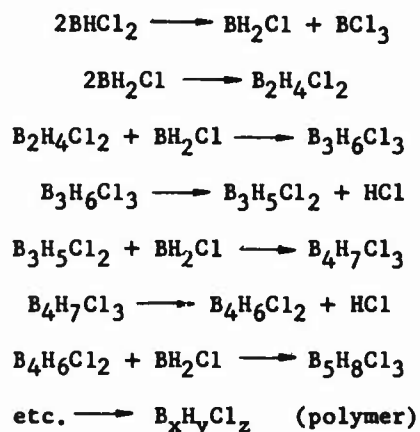
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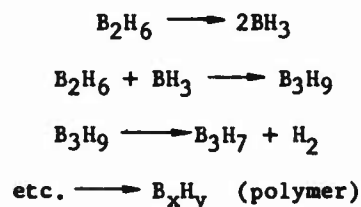
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Because the plant had been designed to avoid the existence of B_2H_6 at temperatures of pyrolysis, the occurrence of these solids was somewhat disturbing. But chemical analysis revealed the presence of 30 to 50 per cent chloride in various samples, and therefore some compound other than B_2H_6 contributed to solids formation.

A possible reaction mechanism for the formation of higher molecular weight chloroboranes could be:



This mechanism is analogous to the B_2H_6 pyrolysis reactions proposed by Schaeffer. (13)



Since only one to two pounds of solids per run were removed from the filters, B_2H_6 yield was not detectedly affected. However, the prevention of accumulations in troublesome spots such as the reactor (1F-1, 1F-2) and reboilers was important to continued operations.

2. Disproportionator (1C-4)

The disproportionation column (1C-4) served two functions: (1) the disproportionation of $BHCl_2$ and (2) the fractionation of the resulting reaction mixture to obtain pure B_2H_6 as the overhead product. While the column itself performed very well, the mechanical problems were substantial in handling the B_2H_6 take-off and reflux. In the first run, no product was taken off; in Run 2, take-off was accomplished only until the pressure in the storage tanks equalized that in the column.

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Initially, reflux was difficult to start because the less dense B_2H_6 could not displace BCl_3 in the gravity reflux system. At the same time, it was found that the $-100^\circ F.$ refrigeration on the reflux and take-off lines, including the product pump (1G-5) was insufficient to prevent flashing and gas binding. The system was reworked to improve refrigeration and permit pumping of the reflux as needed at the start of a run. This aided in producing good results, although runs were not trouble-free.

After an explosion and fire which occurred during Run 10, the reflux and take-off system was redesigned as shown in Figure 61 to provide improved operation and safety. An important feature of the revision was the use of $-100^\circ F.$ refrigeration on one of the B_2H_6 storage tanks (1C-7B) permitting gravity take-off of the product. Troublesome pumping of liquid B_2H_6 was thereby eliminated.

3. Hydrogen Chloride Fractionator

The pilot plant design called for the production of pure anhydrous HCl as the overhead product from the HCl fractionator and pure BCl_3 as the bottoms product. This of course assumed no $BHCl_2$ in the feed so that only HCl and BCl_3 were fractionated in the column. As previously pointed out, essentially pure (99% or better) HCl was produced in many runs, and it is therefore concluded that the column did perform as intended.

During early runs, 4 and 5 in particular, fluctuations in the available plant steam pressure were responsible for much of the product B_2H_6 contamination. A sudden drop in the steam pressure resulted in loss of boil-up in the fractionator reboiler and in dumping of the materials in the column, with subsequent contamination of the fractionator bottoms with HCl . In turn, this caused HCl to go overhead from the secondary absorber (1C-2) and eventually get into the prefractionator (1C-3) feed via the primary absorber (1C-1) stripping gas. Corrective measures were taken regarding the steam supply and, aside from an occasional momentary upset due to an unusual fluctuation, the problem was effectively eliminated during later runs.

4. Diborane Absorber (1C-8)

This column generally performed well and permitted no B_2H_6 to go overhead unless it was slugged with B_2H_6 , such as happened occasionally if the $-100^\circ F.$ refrigeration system failed to keep the B_2H_6 accumulator below $-70^\circ F.$ As mentioned earlier, its original 1/2 inch Intalox saddles were replaced midway in the operating period with 1/4 inch metal Raschig rings. No important changes were noted.

The column usually operated at a higher temperature than design, at 0 to $-10^\circ F.$, rather than the -25 to $-40^\circ F.$ intended. This was strictly a refrigeration problem and could be corrected by installing a $-20^\circ F.$ exchanger in the absorbent line prior to the existing $-50^\circ F.$ exchanger (1E-21).



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D. Refrigeration

As previously indicated, many operating problems were encountered in the refrigeration section. The performance of the packaged refrigeration unit proved to be borderline, particularly during the summer months. Mechanically, the refrigeration unit was generally satisfactory.

Several changes and additions based on operational experience were made to the system during the course of operations:

1. All three compressors were speeded up about 10 to 15 per cent to increase their capacity. In the case of the -20°F. compressor, it was necessary only to change the sheaves since sufficient horsepower was available for the increase in speed. The -50°F. compressor motor was changed from 10 to 15 horsepower and the -100°F. compressor motor from 7.5 to 10 horsepower.
2. The oil reservoir capacity of the system was doubled from 60 to 120 gallons. This was required due to the large pick-up of oil by the refrigerant and failure of the oil regenerator to operate satisfactorily.
3. Additional high pressure storage capacity was added to hold refrigerant during pumpdown. These tanks were barely adequate to hold the refrigerant required for operation. With the pick-up of 60 to 70 gallons of oil in the course of a run, these tanks could not hold the refrigerant-oil mixture during recovery operations, and caused the -20°F. compressor to cut out due to high discharge pressure.
4. An additional -20°F. heat exchanger (1E-23) was added to precool absorbent to the secondary absorber (1C-2). This addition was necessary to remove some of the load from the -50°F. compressor and provide a colder absorbent.
5. A high pressure refrigerant feed line was added to the HCl column condenser to provide a temporary refrigerant supply in the event the refrigerant pump (5G-2) did not have a sufficient head to pump refrigerant to this exchanger.
6. Suction off the pump tank (5C-2) was changed from the -50°F. compressor to the -20°F. compressor to further reduce the load on the -50°F. compressor.
7. Several improvements in insulation and the amount of tracing or jacketing were made to better control process temperatures.

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One of the first problems encountered was the carry-over of liquid to the -20°F. compressor during start-up. This problem was eliminated by the addition of a hand valve between the -20°F. accumulator and the pump tank (5C-2) so that refrigerant would not flow backward between these two tanks and overflow the -20°F. accumulator. This reverse flow only occurred during start-up when the -20°F. compressor was running prior to operation of the -50°F. compressor.

The pick-up of oil by the R-22 refrigerant was much greater than expected. A 2500 pound charge of R-22 would pick up approximately 65 gallons of Capells C oil during five days of operation. This oil is heavier than intended for this service, and while consumption was less than lighter oils originally used, the presence of this oil in the refrigerant caused operating problems in the various evaporators. Much of the refrigeration problem caused by oil in the system was due to the failure of the oil regenerator to effectively separate oil and refrigerant continuously. To distribute the circulating refrigerant to the various heat exchangers in the -20°F. and -50°F. systems, it was necessary to hand throttle the various feed valves. These valves would become oil bound and stop feeding refrigerant. This caused processing problems which had to be corrected by opening the valves wide to flush out the oil and resetting the valve. Problems with this oil were more severe in the -100°F. system as the amount of refrigerant fed to evaporators was only that required by the heat load. Evaporation of the refrigerant left the oil which at -100°F. was very viscous. This interfered with heat exchange, caused control valves to underfeed and overfeed refrigerant, and the thick oil could suddenly close the suction line to the -100°F. compressor causing a heavy loss of -100°F. refrigeration at a critical point in the process. This problem usually occurred after 4 to 5 days of operation.

While the refrigeration system contributed more operational problems than had been anticipated, these were not insurmountable and did uncover sensitive areas which would require careful consideration in a large scale plant design. Again, all the problems were physical ones which can be overcome through proper selection and sizing of equipment.

E. Mechanical Operation

Obviously good mechanical reliability is essential to the successful operation of any plant. This was certainly true in the pilot plant where good performance was required of a number of equipment items in order for the B₂H₆ plant as a whole to function satisfactorily. For example, there were eight pumps and seven compressors (including refrigeration and utilities), each of which was vital, in addition to several control systems and safety devices. Depending on the judgment exercised, a list of 30 to 100 critical items can be compiled, not including such items as motors, starters, columns and exchangers which have either no moving parts or an unquestionably high order of reliability. The expression relating the aggregate reliability (R) to those of the individual members (r), assuming the latter to be equal, is

$$R = (r)^n$$

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where R and r are expressed as decimal fractions and n is the number of items in the aggregate. A few samples follow:

<u>Individual Reliability</u>	<u>Aggregate Reliability</u>	
	<u>30 Items</u>	<u>100 Items</u>
90.0%	4.4%	0.0026%
99.0%	74.0%	36.6%
99.5%	86.0%	60.6%
99.9%	97.2%	90.5%

In view of these facts, it is not surprising that the pilot plant sometimes encountered difficult operation from a mechanical standpoint with a consequent lowering of product purity and yield. In a large scale plant, however, spare units would be provided for the particularly vital and vulnerable elements; thus the aggregate mechanical reliability would be tremendously improved. Considering only the fifteen pumps and compressors mentioned above, the effect of sparing equipment is as follows, again assuming equal reliabilities for all units:

<u>Individual Reliability</u>	<u>Aggregate Reliability, 15 Items</u>	
	<u>No Spared</u>	<u>All Spared</u>
90%	20.5%	74.0%
99%	86.0%	99.85%

In summary, the mechanical reliability of the various equipment items in the pilot plant was probably as good as expected. Even a 99 per cent reliability for individual items would cause intermittent and sometimes inefficient operation typical of the pilot plant experience. However, proper sparing of critical items in a large scale plant would avoid undue difficulties.

Closely akin to the matter of mechanical equipment is the subject of leaks. Despite an elaborate initial test program, some leaks developed in the first test runs as the full range of operating temperatures was attained (-100°F. to + 1300°F.). Some were so small as to be negligible in an ordinary chemical plant; all were corrected, however, because of the hazardous nature of the process materials. As pilot plant operations continued, it was necessary to keep an active program devoted to the correction of leaks which occasionally developed as well as to repair insulation damaged in finding the leaks.

The leaks fell into one of three general classifications: (1) process piping leaks; (2) leaking valves; and (3) leaks along moving shafts. Most of the process piping leaks were associated with lines which were alternately chilled and warmed up to ambient as the result of the intermittent nature of the pilot plant operating schedule. Some developed when equipment was removed and then reinstalled after cleaning or maintenance, or when alterations were made. The practice of silver soldering tubing and screwed fittings proved to be quite satisfactory.

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Valve leaks also occurred principally in refrigerated service. The Jamesbury ball valves originally installed frequently developed stem leaks when operated at -50°F . or below, and these valves had no provision for tightening the stem packing. When these valves were in a cold B_2H_6 line, small fires or minor explosions would result from the leakage. Kerotest globe valves having a diaphragm (packless) stem seal were selected as replacements in the B_2H_6 lines. Operating experience, however, uncovered these shortcomings of the Kerotest valves:

1. The diaphragms sometimes cracked, permitting B_2H_6 to escape.
2. Operators could not tell readily when a valve was open or closed. There was always a tendency to shut off these small valves with excessive force, even to the extent of breaking off the extension handle, with the consequence that reopening was difficult.
3. Insulation mastic sometimes got on the threads of the valve stem, making the valve hard to operate at low temperatures.
4. Shut off was not positive. Undoubtedly the Teflon seat inserts were sometimes damaged by excessive shut off forces.

The failures of these valves to provide a tight shut off caused a serious explosion and fire during Run 10. This incident will be discussed under Safety.

At that time, a survey was made of valves likely to be satisfactory in this difficult application. In addition to performance, important factors considered were fast delivery and cost. Two types of valves were chosen as most suitable: (1) Powell bellows-seal globe valves and (2) standard bonnet Pacific ball valves incorporating a good adjustable stem seal. Both valves proved satisfactory for liquid B_2H_6 service. Later, two extended bonnet Pacific ball valves were tested in the same service and were found to be better than the standard bonnet valves.

Leaks along moving shafts were troublesome in the first several months of operation. In particular, gas leakage along the reciprocating shaft of the Worthington recycle H_2 compressor (1K-1) and BCl_3 leakage through the mechanical seal on the shaft of the Duriron prefractionator bottoms pump (1G-3) required considerable attention. On the former unit, leakage was negligible with fresh carbon ring packing, but the rate increased as boric oxide (or boric acid) was formed by hydrolysis of the trace amounts of BCl_3 present in the recycle gas when it contacted moisture in the air. This problem was solved by keeping a N_2 purge through the distance piece immediately behind the packing. Formation of solids was thereby avoided

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in the vicinity of the packing, and the close fit between the carbon rings and shaft was maintained. Leakage could not be reduced to zero of course, but it was held at an acceptably low level and piped to the destructive scrubber.

The shaft seal leakage on the pump was essentially corrected through a combination of measures: cooling and filtering the seal flushing liquor, providing a cooled bypass on the pump to permit a high pumping rate which minimized shaft deflection, and using a tungsten carbide seal ring. Again, leakage was not always zero, but it was kept at a low level.

Another approach to this problem was the use of a canned pump. An Allis-Chalmers Electric-Cond pump, evaluated in place of the Duriron (1G-3), performed very well initially but developed bearing trouble, a somewhat anticipated fault. Later a leak into the stator windings developed as the result of a gasket failure, causing serious damage.

VI. Safety

No single item received more attention during the design and operation of the pilot plant than the general problem of safety. As previously detailed, all equipment was designed, constructed, and installed in conformance to applicable codes and standards, as well as state and local laws. All safety aspects of the program were stressed during the pilot plant personnel training program presented prior to start-up. Periodic safety training sessions were held during operation of the pilot plant and safe operation was stressed at all times. These efforts resulted in good safety performance.

One serious accident did occur, however. The pilot plant had been shut down after Run 9 to repack the primary and secondary absorbers (1C-1, 1C-2) to modify the pyrolysis plant, and to install additional safety barricades around the B_2H_6 storage tanks. On August 5, the B_2H_6 plant was started up for Run 10. On August 7, a plug was noted in the reflux return line of the disproportionator column (1C-4). The line was isolated by Valves A, B, C and D (Figure 62). These valves were all Kerotest diaphragm globe valves. The isolated line was evacuated and purged from both top and bottom. The suction side of the pump (1G-5) was also evacuated and purged. The reflux return line was then opened at Points, 1, 2, 3 and 4 to determine the location of the plug. This line was traced by $-100^\circ F.$ refrigeration. The refrigeration was shut off after the lines were opened and purged with N_2 . A foreign liquor was noted in these lines and plugs were found in several sections. These plugs disappeared as the line warmed, permitting free passage of the N_2 purge gas. Nitrogen was then blown from the suction side of the B_2H_6 pump (1G-5) to the discharge side and vented out of the quick disconnect fitting in this area. A liquid discharge of alcohol was observed. The B_2H_6 pump was a Lapp Pulsafeeder pump with remote head located in a refrigerated pot containing methanol as the heat transfer fluid.

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Two maintenance men then began to open the refrigerated pot. At this time, the liquid B_2H_6 started to leak from Point 4 (Figure 62) and B_2H_6 gas out of Point 3. Apparently Valve C failed or had previously failed and a plug in the short section of the line between Valve C and the tee into reflux return line gave way, allowing the contents of the disproportionation column (1C-4) to escape to the atmosphere. Failure of the B_2H_6 to ignite instantaneously on escape permitted an explosive B_2H_6 vapor cloud to form before ignition. Blast damage resulted from the ensuing explosion. The ignition delay, however, did permit personnel time to leave the area. All personnel were out of the area with the exception of one maintenance man who was approximately ten yards from the leak at the time of the explosion. He suffered a ruptured ear drum and concussion abrasions, incurring the only lost time injury over the year and a half of the B_2H_6 plant's operation.

The fire was immediately confined and was under control within twenty minutes. However, a small jet flame about four inches long continued at the point of the initial leak for about five hours afterward before it could be sealed off.

Subsequent examination of the B_2H_6 pump (1G-5) revealed a corrosion failure of the suction line adjacent to the remote head located in the chilled alcohol bath. The corroded line (type 304 SS) involved and the fitting (type 316 SS) which connects to the remote head are shown in Figure 63. Apparently the pump had discharged alcohol into the reflux piping. Interaction of the methanol with B_2H_6 and BCl_3 formed products which were solids at the temperature of the refrigerated line, but melted after refrigeration had been turned off. Trimethyl borate, one possible product, has a melting point of $-29^\circ F$. and could have produced the series of occurrences observed.

The corrective actions taken were (1) replacement of all Kerotest diaphragm valves with Pacific ball valves or Powell bellows-seal valves, (2) providing two valves for double shut off at critical locations, and (3) replacement of the methanol in the refrigerated pump pot with less corrosive mineral spirits, immiscible with water.

VII. Analytical Support

The sampling and analysis of the pilot plant streams presented difficulties due primarily to the instability of the process materials in the presence of air. Diborane and dichloroborane burned or exploded on contact with air; boron trichloride reacted with moisture to give HCl and boric oxide. Therefore it was necessary to use special sample containers and high vacuum systems for all sample manipulations. Since nearly every material encountered in the process was toxic and a few were explosive, constant alertness was required on the part of the analysts.

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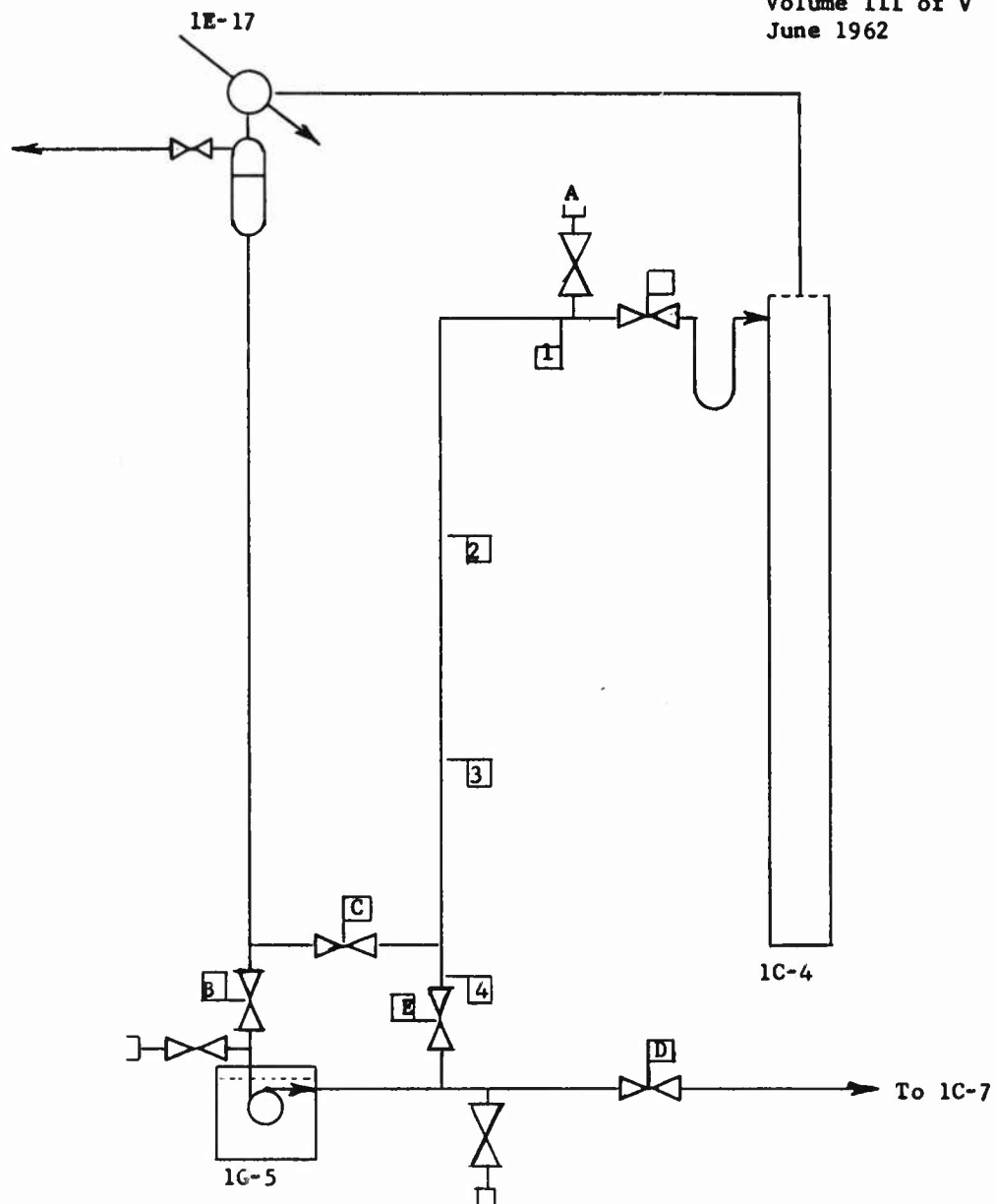


Figure 62. Piping Drawing for Disproportionator Reflux System

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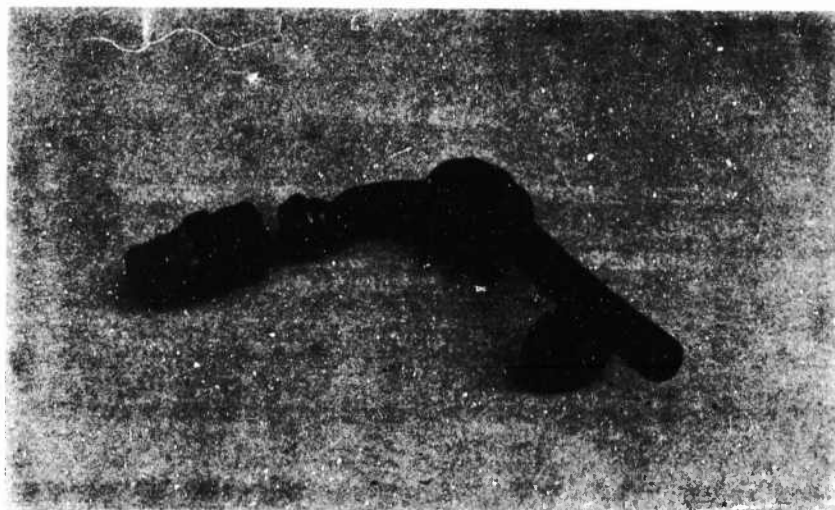


FIGURE 63

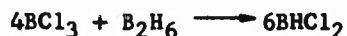
DIBORANE PROCESS. CORRODED PROCESS SUCTION
LINE TO REMOTE PUMP HEAD, PRIMARY CAUSE OF
EVENTS LEADING TO FIRE AND EXPLOSION

C O N F I D E N T I A L

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Adding to the analytical problems was the fact that boron hydride chemistry was a rather new field which made it necessary to develop many of the procedures used. Prior to operation, considerable effort was spent in developing applicable procedures. Most of the components which required repeated routine analysis could be determined by infrared spectrophotometry. Using purified materials, infrared calibration curves were obtained for carbon tetrachloride, phosgene, boron trichloride and diborane. A calibrated curve was also obtained for dichloroborane although this presented a problem since dichloroborane cannot be obtained in the pure state. The dichloroborane used for making the calibration curve was prepared by mixing about 100 mm. pressure of B_2H_6 and 100 mm. of BCl_3 in a previously evacuated glass bulb and allowing it to stand a week at room temperature. During this interval, the following reaction took place to some extent:



The calibration curve for dichloroborane was obtained using this mixture of B_2H_6 , BCl_3 and DCB. The mole per cent BCl_3 and B_2H_6 present were determined using previously obtained curves for these compounds. The mole per cent DCB was then the difference between 100 per cent and the sum of the percentage of B_2H_6 and BCl_3 .

After pilot plant operations began, three unidentified peaks at 6.28, 7.22 and 11.75 microns were noted during infrared analysis of routine samples. The peaks at 6.28 microns and 11.75 microns were seen only occasionally and were seldom of any great magnitude. However, the peak at 7.22 microns was always present and varied greatly in size, the peak being much more prominent in BCl_3 pot bottom samples than in the distilled material. All literature references considered this peak to be one of a closely grouped set of three BCl_3 peaks. However, it was noted that the first two BCl_3 peaks (6.82 and 7.00 microns) remained constant for samples of the same size while the third peak (7.22 microns) varied greatly depending upon the source of the sample. The possibility of this being triboronoxychloride was investigated. Boric oxide was added to BCl_3 and allowed to stand for several days at room temperature. Infrared examination showed no increase in the 7.22 micron peaks under these test conditions. The samples (in steel cylinders) were then heated in boiling water for 15 minutes and allowed to stand overnight at room temperature. Infrared examination of the samples after this treatment did show a decided increase in the 7.22 micron absorbance peaks and furthermore, the increase was proportional to the amount of boric oxide added. This made possible a calibration curve for the weight per cent of boric oxide in BCl_3 . The procedure was repeated with distilled water being added rather than boric oxide. The results were essentially the same in both cases since water reacts with BCl_3 to provide the needed boric oxide. From this point on, the weight per cent boric oxide in BCl_3 was routinely determined on certain samples (primary absorber bottoms, prefractionator bottoms, HCl fractionator bottoms, and reactor effluent).

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The determination of small amounts of HCl in the presence of BCl_3 was unsatisfactory. The infrared absorption peaks were too weak to be useful unless HCl were present to the extent of 20 mole per cent or better. Even at these higher concentrations, results were never too accurate because of the extremely large factor employed (weak absorption necessitates a large factor). Also, attempts to determine the HCl content of BCl_3 by hydrolyzing the BCl_3 and determining the chloride to boron ratio were not entirely successful. Attempts to separate HCl from BCl_3 by gas-liquid chromatography were unsuccessful even though a number of column materials and operating conditions were investigated.

Since all BCl_3 feed material required analysis for silicon and free chlorine, procedures were developed for these analyses. Before the BCl_3 could be analyzed for these components, a hydrolysis was necessary. A special apparatus was constructed to effect a liquid transfer under vacuum from the sample cylinder to a weighed reaction tube. Extreme caution was exercised in the weighing and hydrolysis of the BCl_3 . Once hydrolyzed, the chlorine and silicon were determined colorimetrically using modifications of the o-tolidine and silicomolybdic acid methods, respectively.

By hydrolyzing a diborane sample in an alcohol-sodium hydroxide solution and titrating the chloride by the Volhard method, HCl in B_2H_6 was determined. Infrared methods could not be used because of the previously mentioned weakness of the HCl absorption peaks. Also, these peaks were partially obfuscated by the 3.83 micron B_2H_6 peak.

Table 59 lists the points sampled during routine operations, the components sought and the normal method of analysis. As shown, the majority of samples were analyzed by infrared absorption spectrophotometry using a Beckman IR-4 Spectrophotometer. Both liquid and gas samples were analyzed by infrared methods for diborane (B_2H_6), dichloroborane (BHCl_2), boron trichloride (BCl_3), triboronoxychloride ($\text{B}_3\text{O}_3\text{Cl}_3$), and hydrogen chloride (HCl), the latter only if present to the extent of about 20 mole per cent or better. Also, BCl_3 fractionator column bottoms and tops were analyzed by infrared methods for phosgene (COCl_2) and carbon tetrachloride (CCl_4). Table 60 lists the components determined by infrared and the wavelengths in microns of the absorption peaks used in the calculations.

TABLE 59
Step I Sample Points and Analyses

Sample Point	Designation	Analyses	Method
Primary Absorber Bottoms	1C-1B	B ₂ H ₆ , BHCl ₂ , BCl ₃ , (BOCl) ₃	IR
Primary Absorber Overhead	1C-1T	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
Secondary Absorber Overhead	1C-2T	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
Prefractionator Bottoms	1C-3B	B ₂ H ₆ , BHCl ₂ , BCl ₃ , (BOCl) ₃	IR
Prefractionator Overhead	1C-3T	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
HCl Fractionator Bottoms	1C-5B	B ₂ H ₆ , BHCl ₂ , BCl ₃ , (BOCl) ₃	IR
HCl Fractionator Overhead	1C-5T	B ₂ H ₆ , BHCl ₂ , BCl ₃ , HCl	IR
B ₂ H ₆ Absorber Feed	1C-8F	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
B ₂ H ₆ Absorber Overhead	1C-8T	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
HCl Product Tank	1C-9	B ₂ H ₆ , BHCl ₂ , BCl ₃ , HCl	IR
Disproportionator Reflux (B ₂ H ₆ Product)	1C-4R	B ₂ H ₆ , BHCl ₂ , BCl ₃	IR
Disproportionator Reflux (B ₂ H ₆ Product)	1C-4R	HCl	Hydrolysis + Wet
BCl ₃ Fractionator Column Bottoms	4C-2AB	COCl ₂ , CCl ₄	IR
BCl ₃ Fractionator Column Overhead	4C-2AT	COCl ₂ , CCl ₄	IR
Pure BCl ₃ Storage	4C-4A	COCl ₂ , CCl ₄ , (BOCl) ₃	IR
Pure BCl ₃ Storage	4C-4B	COCl ₂ , CCl ₄ , (BOCl) ₃	IR
Pure BCl ₃ Storage	4C-4C	COCl ₂ , CCl ₄ , (BOCl) ₃	IR
BCl ₃ TRONA Cylinders	-	BCl ₃ , COCl ₂ , CCl ₄ , (BOCl) ₃	IR
BCl ₃ TRONA Cylinders	-	Cl ₂ , S ₁	Hydrolysis + Colorimetric

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TABLE 60

Infrared Absorption Peaks Used for Calculation

Component	Wavelength (microns)
BCl_3 (high conc.)	5.22
BCl_3 (low conc.)	10.06
BHCl_2	9.12
B_2H_6 (high conc.)	5.32
B_2H_6 (low conc.)	6.23
$\text{B}_3\text{O}_3\text{Cl}_3$	7.22
HCl	3.38
COCl_2	11.77
CCl_4	12.56

The determination of HCl in B_2H_6 product by hydrolysis and wet methods proved a very reliable procedure as were the colorimetric procedures for silicon and chlorine.

After sampling and analytical procedures had been developed, an intensive training program for all analytical personnel was provided. The following subjects were included: general background of the project, the chemistry of the AFN process, the nature of the materials to be encountered, safety aspects, plant operation, sampling techniques and equipment, and analytical procedures. Much of the later success of the analytical program can be attributed to this very thorough initial training program. Intermittent pilot plant operations allowed time for various non-routine analytical tasks and equipment repair.

During one shutdown period, an investigation was made of the possibilities of separating BCl_3 from phosgene by treatment with two solid absorbing agents, activated charcoal and Linde Molecular Sieve. Neither reduced the phosgene level.

The possibility of reaction of phosgene with B_2H_6 was also investigated by placing one mmole BCl_3 containing 0.11 per cent phosgene in a 500 cc. stainless steel cylinder containing one mmole B_2H_6 and holding at 45°C for 17 hours. Infrared analysis showed no significant change in phosgene and no new peaks except the expected dichloroborane peaks resulting from the reaction of BCl_3 and B_2H_6 .

Another time, a method was developed for the estimation of boron-hydrogen bonding in polymeric materials. The method was based on the

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infrared absorption at 3.8 microns due to boron-hydrogen bonding. The absorbance was used to determine the equivalent weight of decaborane that would absorb to the same extent. Assuming (1) that the absorbance per boron-hydrogen bond in polymer (BH_x) is the same as for decaborane ($B_{10}H_{14}$), and (2) that the number of boron-hydrogen bonds per unit weight is essentially the same for polymer as for decaborane, then the amount of polymer in the solid sample could be estimated. Various weights of decaborane were mixed with potassium bromide, pelletized and IR spectra obtained. The absorbance of the 3.8 micron peak was calculated for each sample. The boron-hydrogen bonding solids could then be estimated by mixing a known weight of the solid with the same weight of potassium bromide as was used in preparing the standard curves for decaborane. The mixture was pelletized and an IR spectrum obtained. The milligram equivalent of decaborane was determined from the absorbance with the aid of the curve. The results were considered as estimates of the degree of boron-hydrogen bonding in samples. The potassium bromide pelleting technique itself plus the unstable nature of some of the samples precluded highly precise results.

Other special tests and analyses were carried out, including testing of hoses, lubricants, etc. for resistance to BCl_3 and the boron hydrides; obtaining freezing points and IR spectra of various materials; analyzing polymer for boron and chloride; checking calibration curves, etc.

Detailed descriptions of the analytical methods, sampling procedures, apparatus and equipment can be found in Appendix L.

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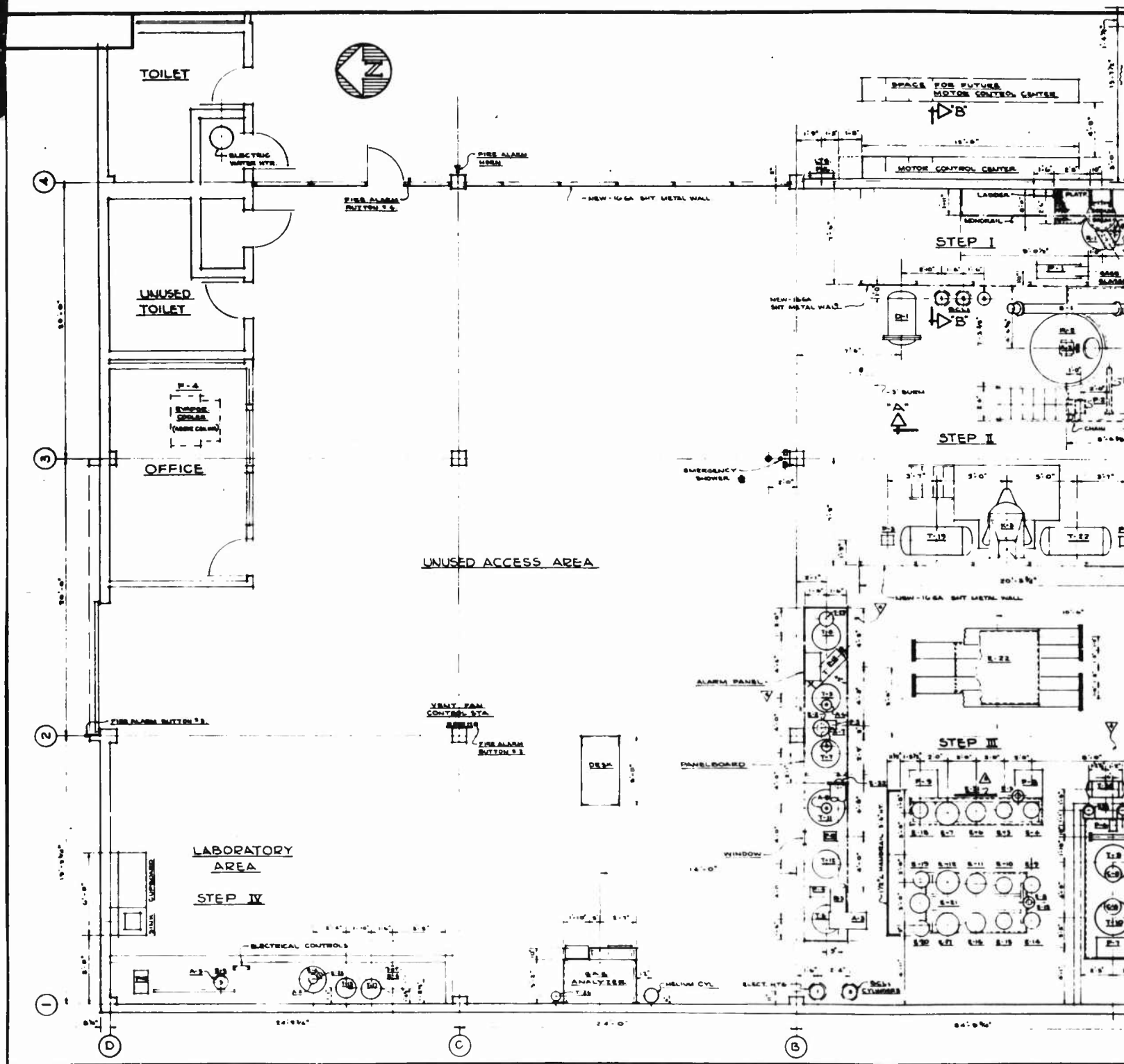
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APPENDIX A

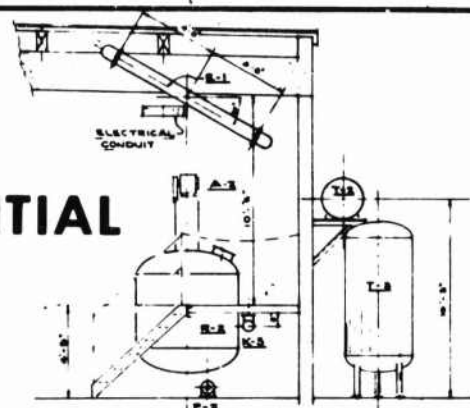
Prepilot Plant
General Arrangement and Heat Balance Flowsheets

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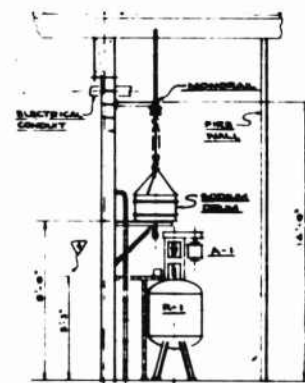
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SECTION "A-A"



SECTION "B-B"

**APPROVED
FOR
CONSTRUCTION**

FIGURE A-1
GENERAL ARRANGEMENT -
HENDERSON PREPILOT PLANT

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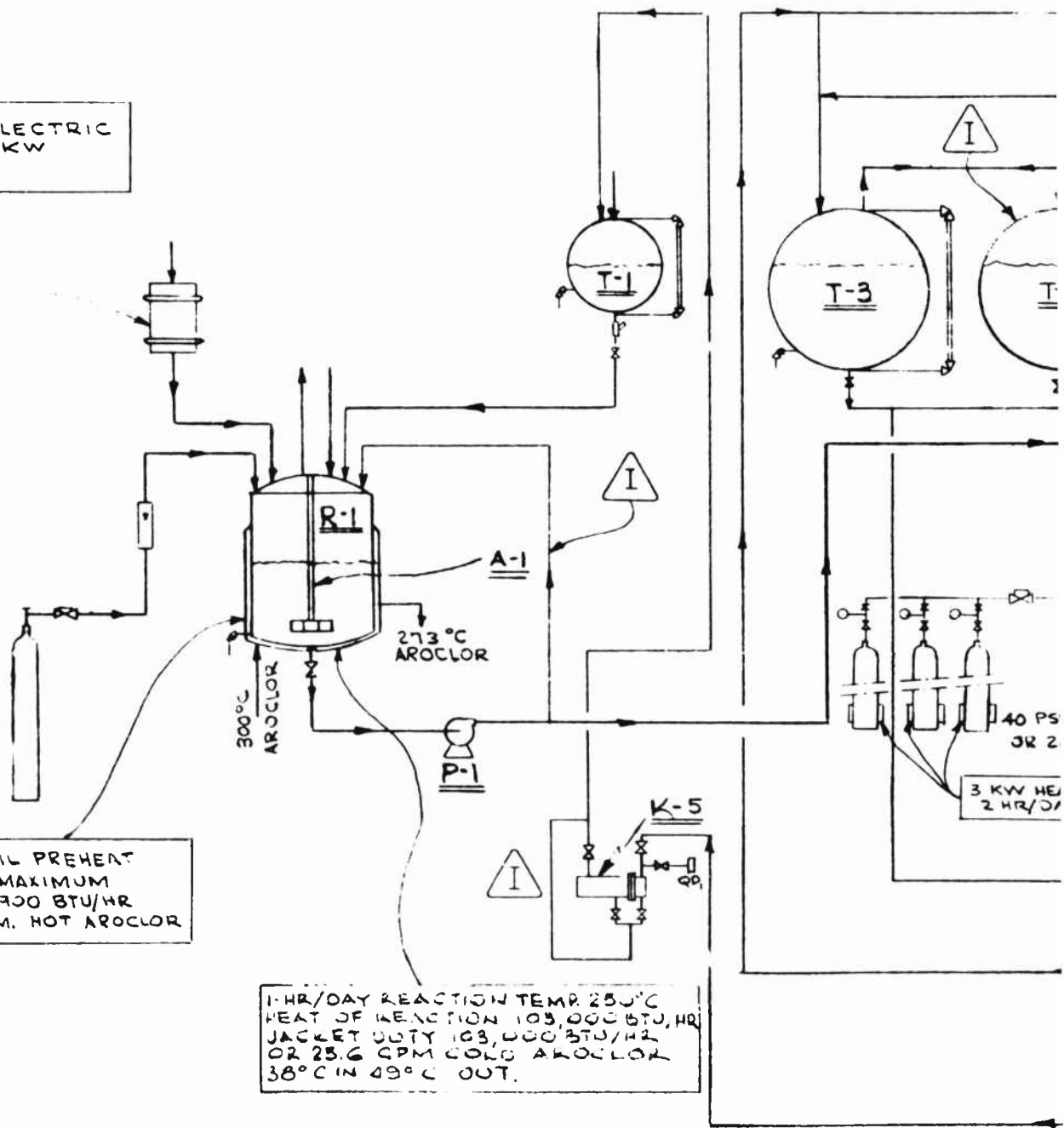


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DRUM HEATERS, ELECTRIC
1 HR/DAY AT 2.5 KW

REACTOR + OIL PREHEAT
1-HR/DAY AT MAXIMUM
DUTY = 205,900 BTU/HR
OR 19.5 G.P.M. HOT AROCLOR

1-HR/DAY REACTION TEMP. 250°C
HEAT OF REACTION 103,000 BTU/HR
JACKET DUTY 103,000 BTU/HR
OR 25.6 GPM COLD AROCLOR
38°C IN 49°C OUT.



1

2-HR/DAY OPERATION
DUTY 182,400 BTU/HR.
OR 18.3 G.P.M. COLD WATER.

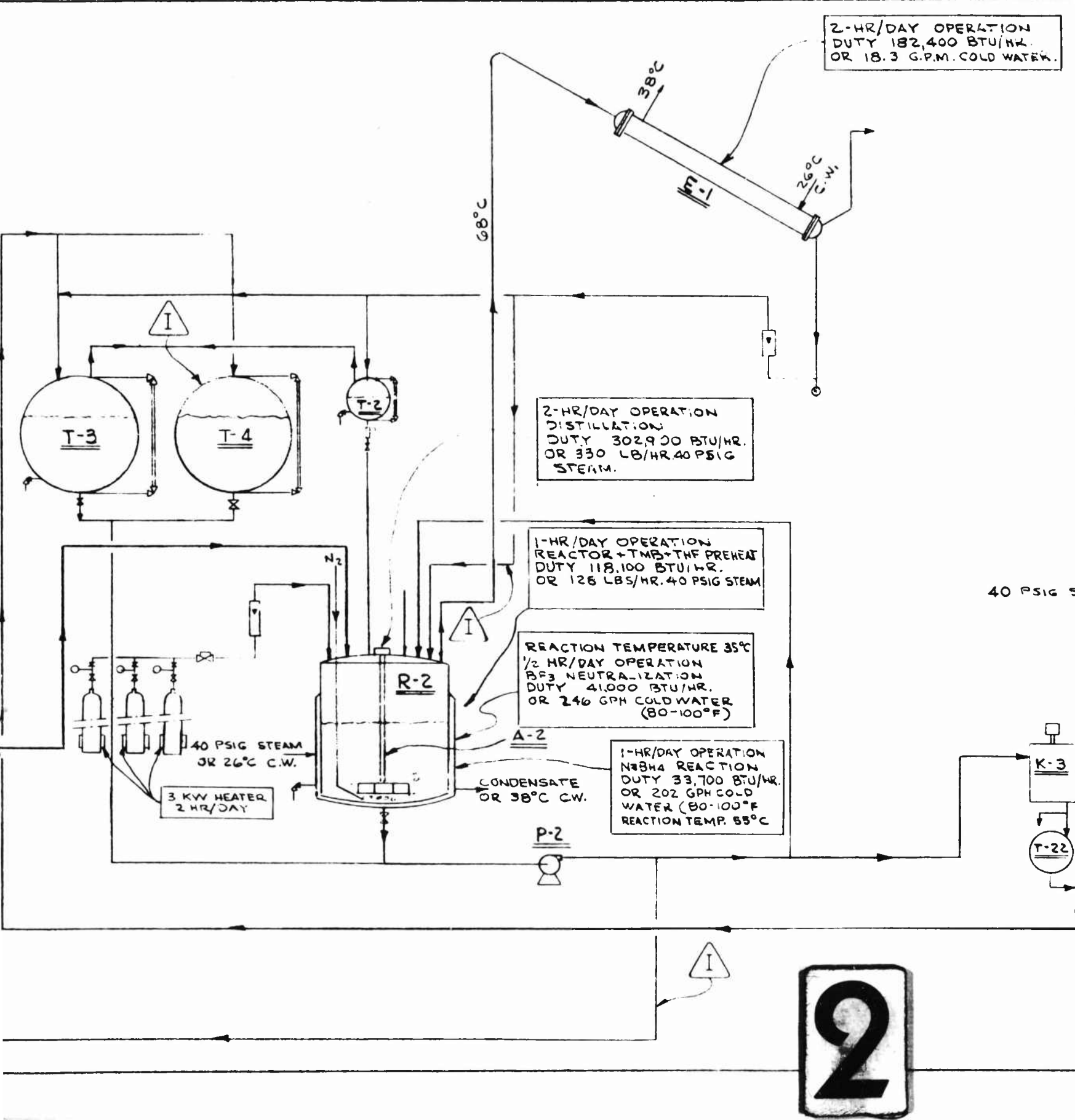
2-HR/DAY OPERATION
DISTILLATION
DUTY 302,900 BTU/HR.
OR 330 LB/HR. 40 PSIG
STEAM.

1-HR/DAY OPERATION
REACTOR + TMB + THF PREHEAT
DUTY 118,100 BTU/HR.
OR 126 LBS/HR. 40 PSIG STEAM

REACTION TEMPERATURE 35°C
1/2 HR/DAY OPERATION
BF₃ NEUTRALIZATION
DUTY 41,000 BTU/HR.
OR 246 GPH COLD WATER
(80-100°F)

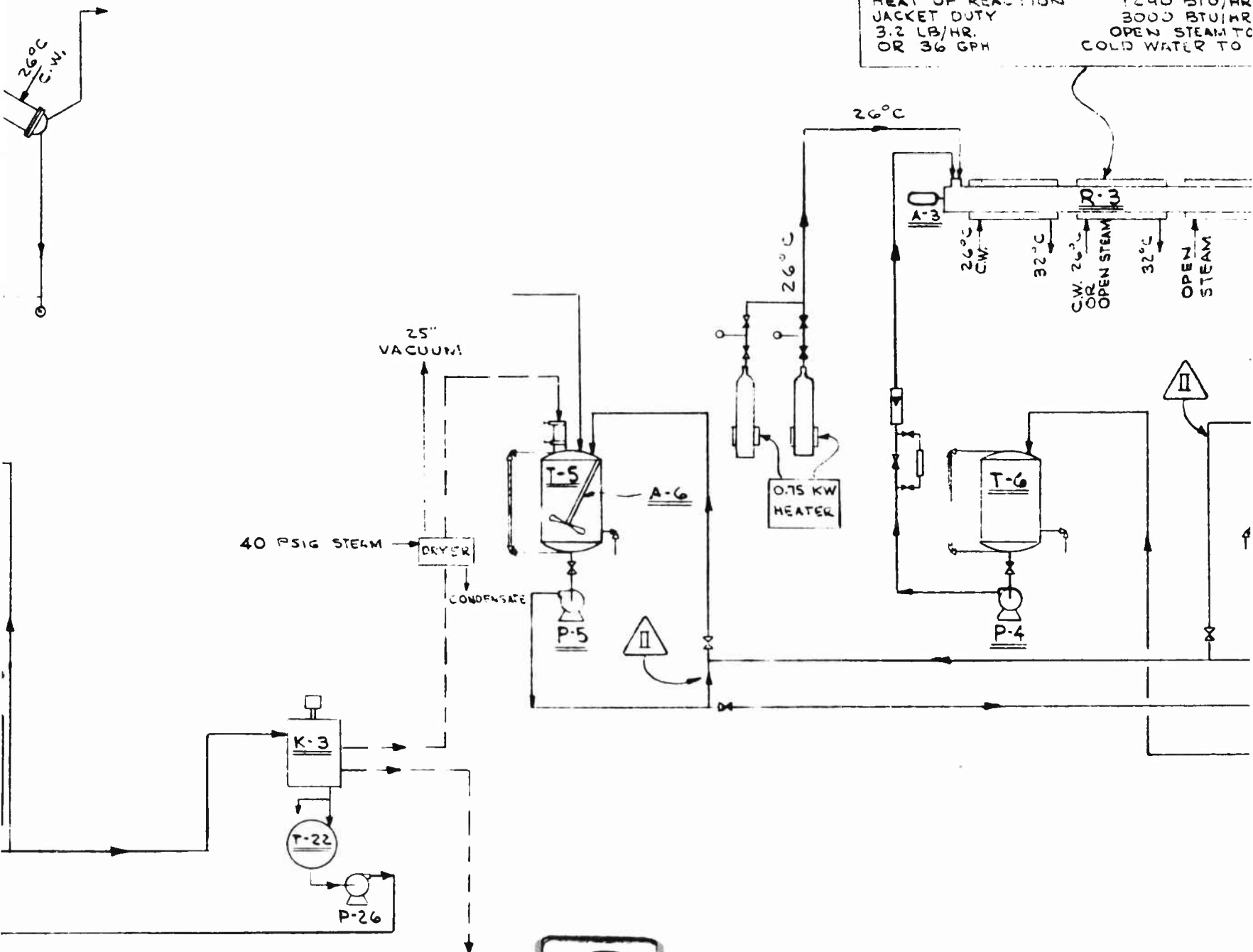
1-HR/DAY OPERATION
N₂BH₄ REACTION
DUTY 33,700 BTU/HR.
OR 202 GPH COLD
WATER (80-100°F
REACTION TEMP. 55°C

40 PSIG S



2-HR/DAY OPERATION
DUTY 182,400 BTU/HK.
OR 18.3 G.P.M. COLD WATER.

CONTINUOUS OPERATION
HEAT OF REACTION 1290 BTU/HR
JACKET DUTY 3000 BTU/HR
3.2 LB/HR. OPEN STEAM TO
OR 36 GPH COLD WATER TO



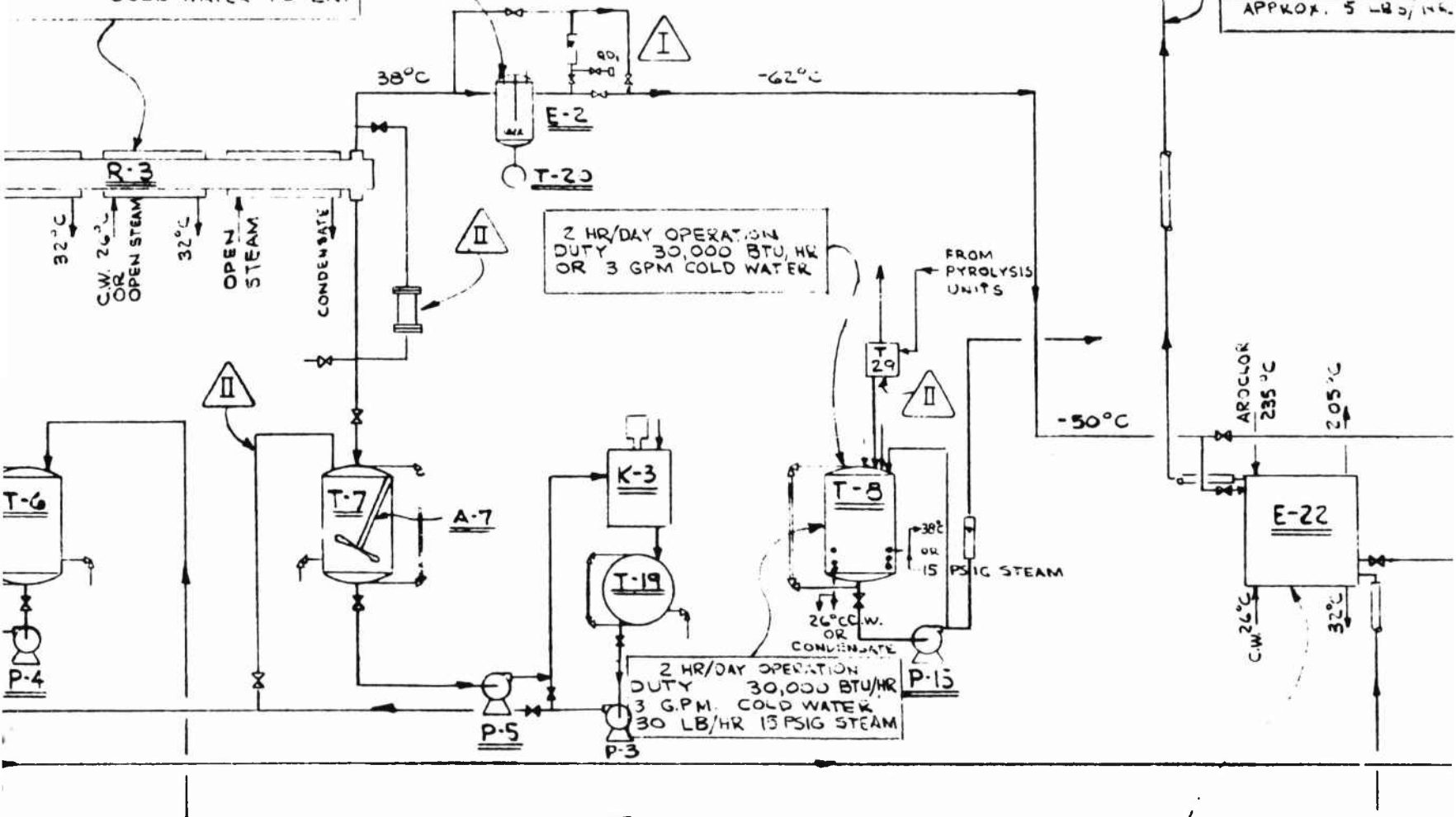
3

CON

CONTINUOUS OPERATION
ACTION 1290 BTU/HR.
3000 BTU/HR. EA.
OPEN STEAM TO EA.
COLD WATER TO EA.

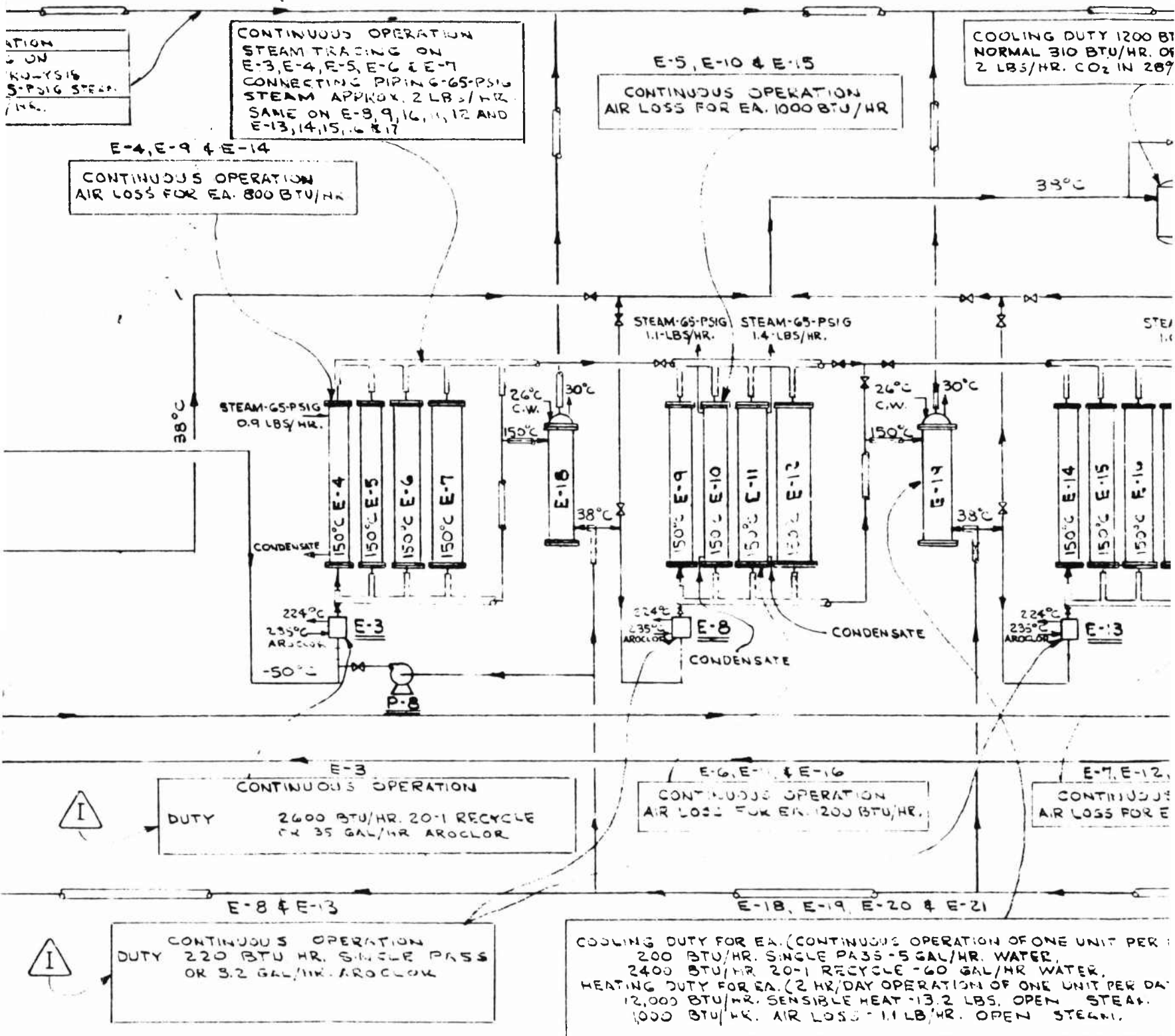
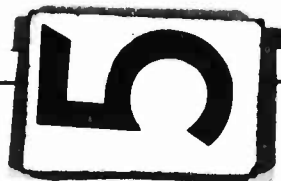
CONTINUOUS OPERATION
COOLING DUTY 700 BTU/HR. @ -75 °C
NORMAL -150 BTU/HR OR 1 LB/HR CO₂ IN ACETONE

2 HR/DAY OPERATION
STEAM TRACING ON
LINES FROM PYRO-
UNITS TO T-11-S-P-
APPROX. 5 LBS/HR.



4

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COOLING DUTY 1200 BTU/HR @ -40°C
 L 310 BTU/HR. OR APPROXIMATELY
 1/2 HR. CO₂ IN 20% C₂H₅ SOLUTION

COOLING DUTY 2400 BTU/HR @ -80°C
 NORMAL DUTY OF 500 BTU/HR WITH LOSSES
 OR 2 LBS/HR CO₂ IN ACETONE

33°C

E-24

-35°C

E-33

-10°C

C-2

26°C

C-3

II

STEAM-63 PSIG
 1.6 LBS/HR.

150°C E-14
 150°C E-15
 150°C E-16
 150°C E-17

E-13

CONDENSATE

26°C C.W.

30°C

E-20

38°C

E-21

CONDENSATE

OPEN STEAM

T-9

P-6

K-4

I

30

T-10

P-7

E-7, E-12, & E-17

CONTINUOUS OPERATION
 AIR LOSS FOR EA. 1400 BTU/HR.

2 HR/DAY OPERATION
 DUTY 2500 BTU/HR.

125°C

300°C
 AROCLOR
 140 LBS/HR

E-21

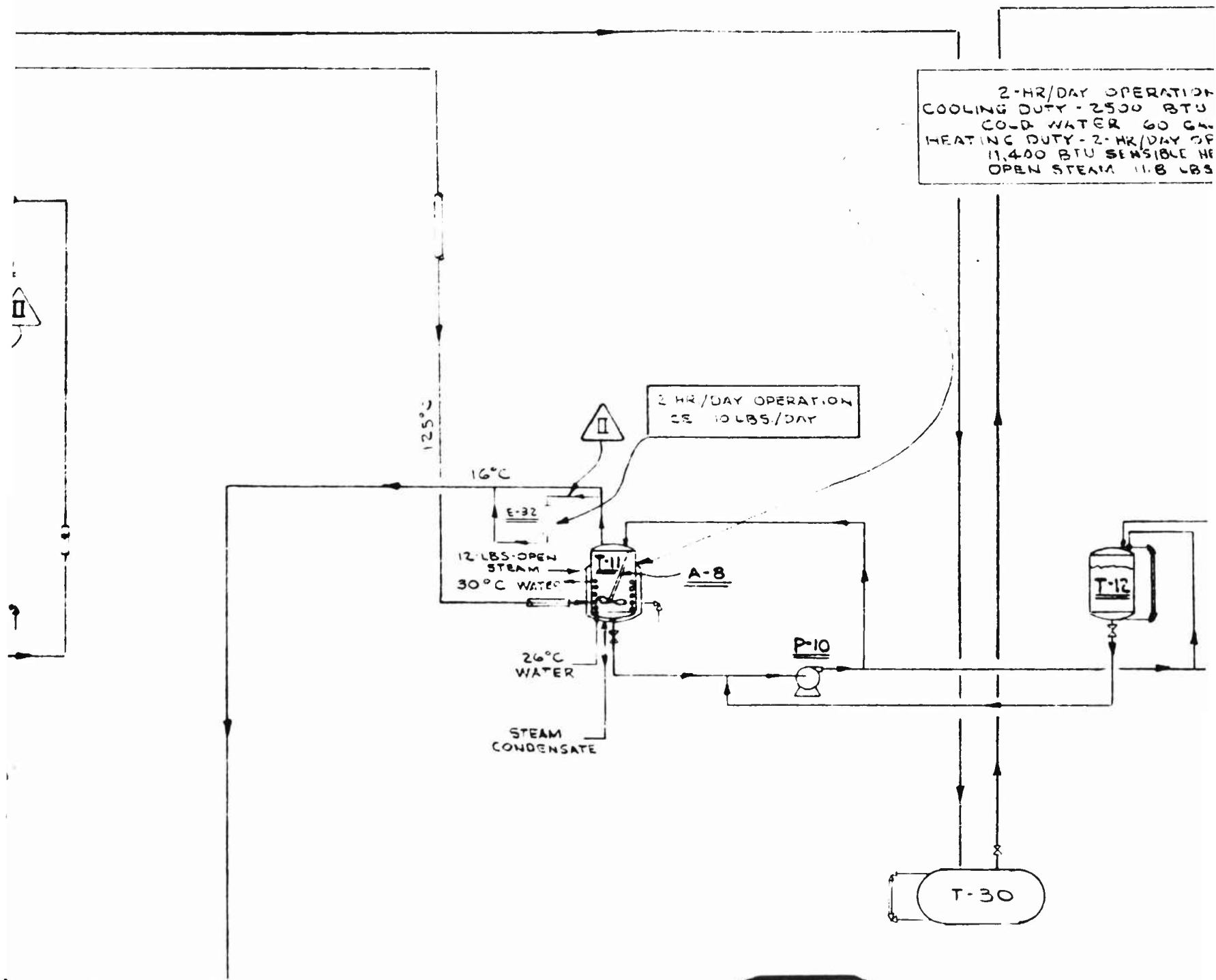
272°C

P-9

21°C

(ONE UNIT PER DAY)
 P. WATER.
 (ONE UNIT PER DAY)
 I. STEAM.
 STEAM.

6

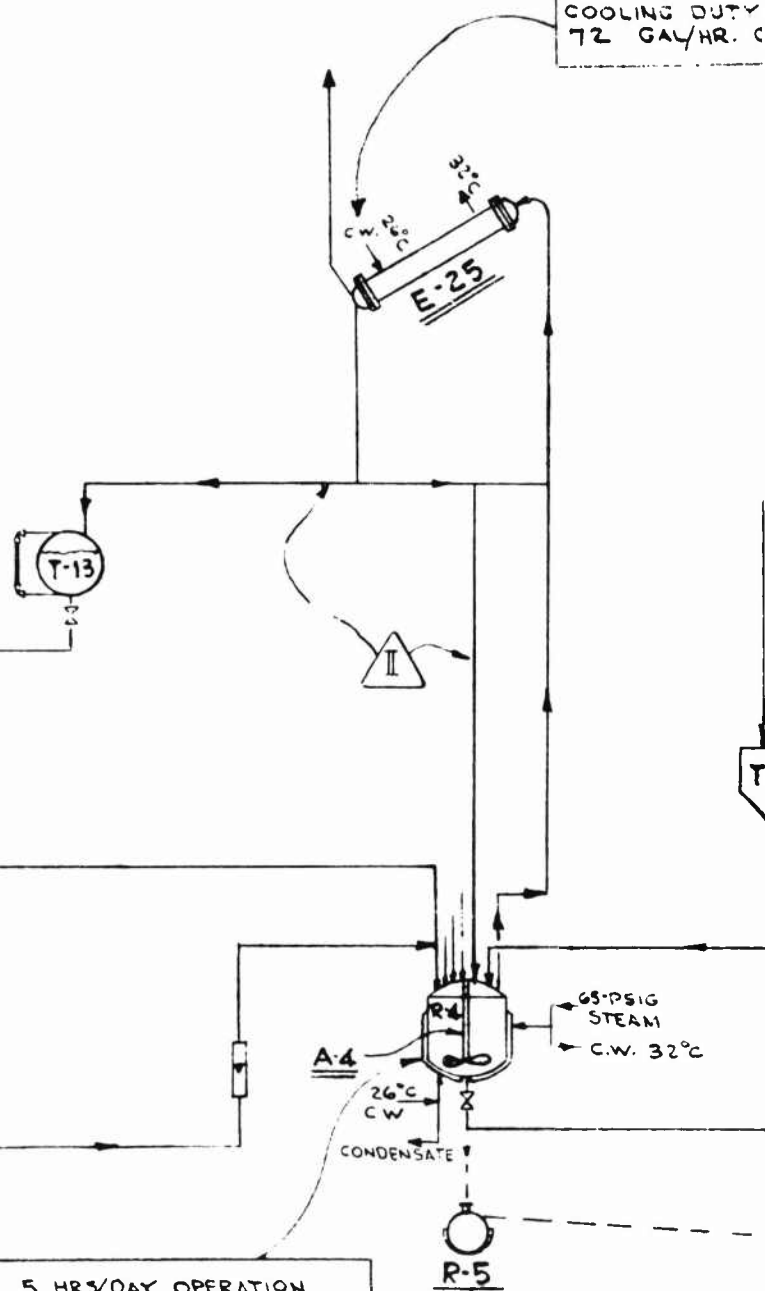


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7

OPERATION
 5 BTU/HR.
 60 GAL/HR.
 1/DAY OPERATION
 SENSIBLE HEAT TO 55°C
 11.8 LBS.

COOLING DUTY
 72 GAL/HR.



5 HRS/DAY OPERATION
 REACTION TEMP. 55°C
 DUTY 7000 BTU/HR.
 7.5 LB/HR. 15 PSIG STEAM
 COOLING
 SENSIBLE HEAT 3000 BTU/HR
 DUTY 6000 BTU/HR
 COLD WATER 2 GPM FOR 0.5 HRS.

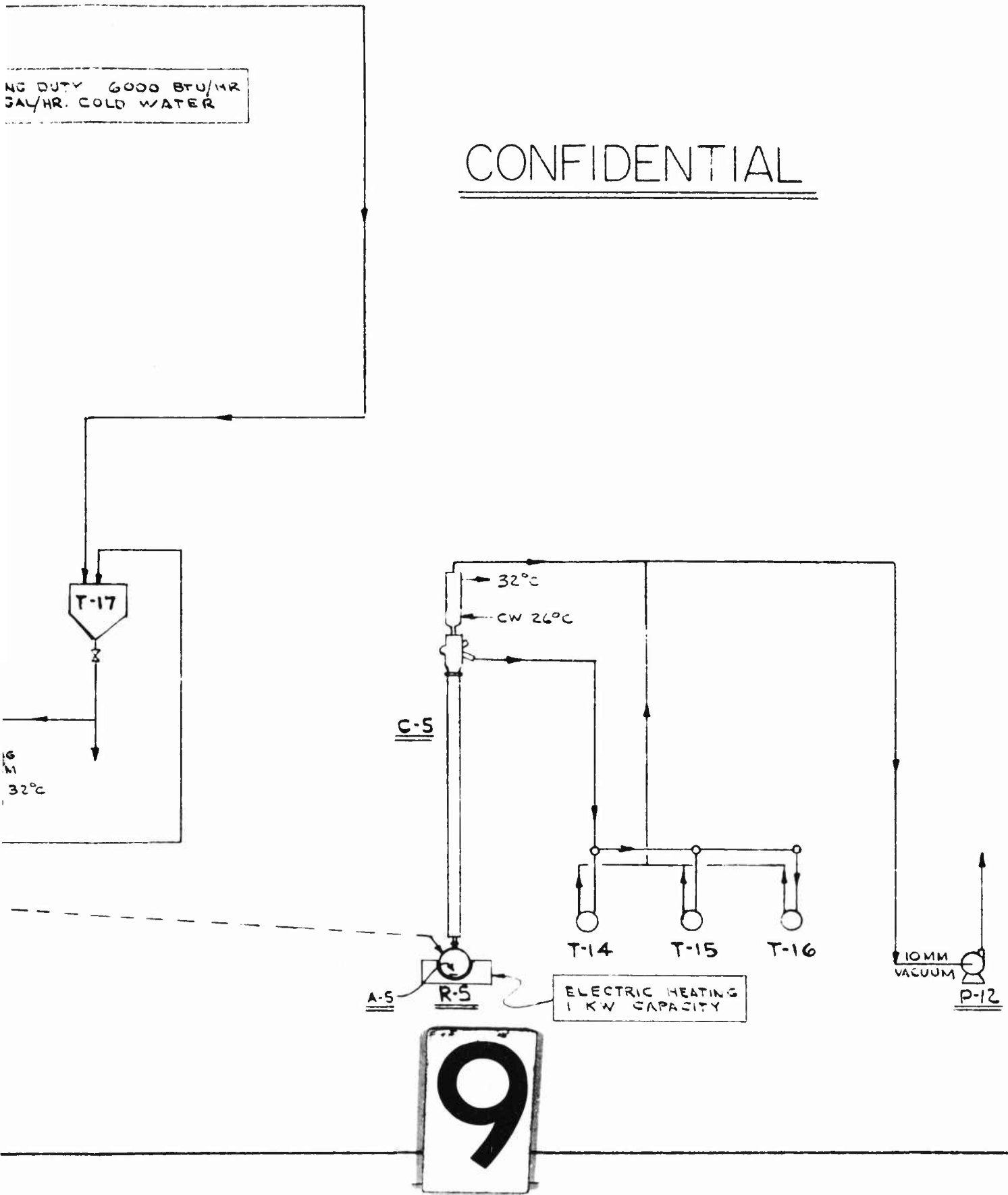
8

NO DUTY 6000 BTU/HR
GAL/HR. COLD WATER

NOTES

1.
2.

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REV-2- <u>II</u> 3
REV-1- <u>I</u> 1-2
REV-C 12-27
DATE 12-26-57
SCALE NONE

NOTES:

1. CONTINUOUS OPERATION BASED ON 20 HR. DAY
2. OPERATION OF PYROLYSIS UNITS ASSUMES CONTINUOUS OPERATION OF EITHER ONE HOT-COLD UNIT OR THE THREE STAGE REACTOR-CONDENSER UNIT.

10MM
VACUUM



P-12

REV-2- 	3-14-58	
REV-1- 	1-27-53	
REV-C	12-27-57	

10

AMERICAN POTASH & CHEMICAL CORPORATION
RESEARCH ENGINEERING

DATE 12-26-57	DRAWN E. PHILLIPS
SCALE NONE	APPROVED 

HEAT BALANCE FLOWSHEET-A.F.M.
HENDERSON PREPILOT PLANT

DRAWING NO.
110-FM-2

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APPENDIX B

Analytical Procedures

Prepilot Plant - Sodium Route

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APPENDIX B

Analytical Procedures

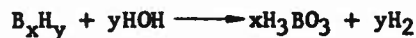
PREPILOT PLANT - SODIUM ROUTE

I. Chemical Methods

A. Determination of Alkalinity, Total Boron, and Sodium Chloride in Ansul Ether-NaBH₄ Feed and Spent Solutions and Filter Cakes

General Discussion

Total alkalinity and total boron are determined by converting the sodium borohydride and other compounds in samples for the feed or spent stream of the diborane generator to sodium hydroxide and boric acid, i.e.



The alkalinity may be titrated with standard acid while the boric acid in the presence of mannitol may be titrated with standard base. The chloride present is titrated with standard silver nitrate solution to a silver chromate endpoint.

Reagents

0.1 N standard hydrochloric acid
0.1 N standard sodium hydroxide
0.1 N silver nitrate
Methyl red indicator
Phenolphthalein indicator
Reagent grade mannitol
1% sodium chromate solution

Sample Preparation

Weigh 5 to 6 grams sample into a 100 ml. volumetric flask, add 50 ml. water and swirl; allow the sample to stand until all gas evolution has ceased and all solid material is dissolved. Dilute to mark.

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Procedure

Alkalinity and Boron

Pipette duplicate 10 ml. aliquots of the prepared sample solution into 250 ml. Erlenmeyer flasks containing 50 ml. of water. Add 5 drops of methyl red and over-titrate the alkalinity present in the sample to an excess of 5 ml. of N/10 hydrochloric acid. Heat the samples and allow to boil for not more than one minute; cool, and back-titrate the excess acid with N/10 sodium hydroxide. Record the net volume of acid used as the alkalinity value.

Add 8 drops of phenolphthalein and add a volume of N/10 sodium hydroxide calculated to be a slight excess. Heat the solutions and boil for one minute; cool to room temperature, add 6-8 grams of reagent grade mannitol and titrate with N/10 hydrochloric acid to a neutral phenolphthalein endpoint. Record the net volume of sodium hydroxide used as the boric acid acidity value.

Calculations

$$\frac{(\text{ml. HCl})(N \text{ HCl})}{\text{Sample Wt.}/10} = \text{meq./gm. alkalinity}$$

$$\frac{(\text{ml. NaOH})(N \text{ NaOH}) 1.082}{\text{Sample Wt.}/10} = \% \text{ total boron}$$

Sodium Chloride

Pipette duplicate 10 ml. aliquots of prepared sample solution into 250 ml. Erlenmeyer flasks containing 50 ml. of water. Add one ml. concentrated nitric acid and heat the sample solutions to boiling. Allow the solutions to boil for five minutes, cool and neutralize the excess acid with calcium carbonate. Add ten drops of sodium chromate and titrate to the first silver chromate color change (brick red). Record the volume of N/10 silver nitrate used. Run a titration on the reagents used, correct the sample titration for any reagent blank.

Calculations

$$\frac{(\text{ml. AgNO}_3)(N \text{ AgNO}_3) 5.845}{\text{Sample Wt.}/10} = \% \text{ NaCl}$$

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B. Determination of Boron in Soluble Borates

General Discussion

The addition of mannitol to a neutral, unbuffered solution of borates causes the solution to become acid. The quantity of standard alkali required to titrate the solution back to a phenolphthalein endpoint is an accurate measure of the boron present.

Sample Preparation

This procedure may be used to determine boron in samples from any product in which the boron can be converted to a soluble borate. After conversion of the boron to a borate, the procedure may be followed exactly.

Reagents

HCL Standard 0.1 N
NaOH Standard 0.1 N
Methyl red indicator, 0.01% aqueous solution
Phenolphthalein indicator, 1% in 70% Ethanol
Mannitol, reagent grade

Procedure

Transfer an aliquot of the solution to be analyzed to a 250 ml. narrow mouth Erlenmeyer. Adjust the pH to the methyl red neutral point or to a pH of 5.3 if a pH meter is available, with N/10 NaOH or N/10 HCl, then add 5 ml. HCl in excess. Add a few glass beads and boil for three minutes to expel CO₂, cool and neutralize again to the methyl red neutral point or to a pH of 5.3 with N/10 NaOH. Add 6-8 grams of mannitol, 10 drops of phenolphthalein indicator and titrate with N/10 NaOH to the first phenolphthalein pink coloration or to a pH of 8.0 and record the titration. Run a blank with the reagents alone following the above procedure and correct the titration for the reagent blank.

Calculations

$$\frac{(\text{ml. NaOH})(N \text{ of NaOH})(1.082)}{\text{Sample Wt.}} = \% \text{ Boron}$$

Comments

It is important that all boron in the sample be in the form of soluble borate. Otherwise low results will be obtained. If boron is present in other forms, it must be converted to soluble borate before titration. In the case of T-8 caustic scrubber solutions, this is best done by heating with nitric and perchloric acids.

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C. Determination of Boron and Carbon in Boron Carbide

General Discussion

Boron in boron carbide is determined by converting the boron to a soluble sodium borate by fusion in a mixture of sodium carbonate and sodium nitrate. The sodium borate is converted to boric acid with hydrochloric acid and titrated with standard sodium hydroxide in the presence of mannitol. Carbon in boron carbide is determined indirectly by refluxing with 1:3 nitric acid, weighing the residue and determining the amount of boron in the residue. Since the residue consists of boron carbide plus free carbon, the carbon is the difference between the nitric acid insoluble residue and the boron content of the nitric acid insoluble residue corrected for the amount of nitric acid soluble material.

Sample Preparation

Crush a representative sample of boron carbide to minus 60 mesh in a diamond mortar.

Determination of Boron

Transfer 0.10 to 0.15 gram of sample to a tared platinum crucible and weigh to the nearest 0.1 milligram. Add approximately 1.5 grams of sodium carbonate and mix well with a well-rounded, thin, dry glass rod, taking care that no part of the mixture adheres to the rod after mixing is complete. Cover the crucible and heat with a low, relatively cool flame of a Fisher burner for approximately 5 minutes, taking care to avoid loss by splattering or frothing. Gradually increase the heat to fuse the mixture and hold at the fusion temperature for five minutes. Cool. Add 100 to 200 milligrams of sodium nitrate, cover the crucible, and fuse for an additional 20 minutes. Cool and dissolve the melt by placing the crucible and cover in a covered 400 ml. beaker containing 50 ml. of 1:1 hydrochloric acid. When digestion is complete, remove and wash the crucible and cover, combining the washings with the solution. If the solution is not clear, filter off the solid material and discard it.

Transfer the solution to a 250 ml. volumetric flask and dilute to the mark. Pipette a 50 ml. aliquot into a 250 ml. Erlenmeyer flask, add 3 drops of methyl red indicator (0.02% water soln. of water soluble methyl red) and neutralize the excess hydrochloric acid with 25% sodium hydroxide solution.

(Boron carbide may contain iron or other impurities which interfere with the mannitol-phenolphthalein endpoint. If such impurities are present, add 2-3 gms. barium carbonate (Baker & Adamson Reagent No. 1404) to the neutralized aliquot. Swirl the flask gently and allow the suspended material to settle. Filter through a medium paper (Whatman No. 40, or equivalent) and wash thoroughly with distilled water.)

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Adjust the pH to the methyl red neutral point with N/10 sodium hydroxide or N/10 hydrochloric acid, whichever is necessary, and then add 5 ml. N/10 hydrochloric acid in excess. Add a few glass beads and boil for 3 minutes to expel carbon dioxide, cool in a water bath, and again neutralize to the methyl red neutral point with carbon dioxide free N/10 sodium hydroxide. Add 6-10 grams of reagent grade mannitol, 20 drops of phenolphthalein indicator and titrate with N/10 sodium hydroxide to the first phenolphthalein pink coloration. Record this titration as the uncorrected boron titration. Run a blank with the reagents alone, following the above procedure exactly and correct the above titration for the reagent blank.

Calculate the percent boron from the corrected titration as follows:

$$\frac{(\text{ml. NaOH})(N \text{ of NaOH})(1.082)}{\text{weight of sample}} = \% \text{ boron}$$

Determination of Carbon

Weigh approximately 0.500 gram of sample to the nearest 0.001 gram and transfer to a 250 ml. boiling flask equipped with a standard taper glass connection and a vertical, water-cooled reflux condenser. Add 100 ml. of 25 per cent nitric acid (1 part concentrated nitric acid and 3 parts water by volume). Swirl and allow to stand at room temperature for approximately 20 minutes, and then reflux for 2 hours.

Cool and filter the solution through a tared sintered glass crucible (fine porosity). Wash the insolubles with hot water, dry at 110°C for one hour, and weigh.

Calculate acid insoluble matter from the gain in weight of the crucible as follows:

$$\frac{(\text{grams insolubles})(100)}{(\text{grams sample})} = \% \text{ insolubles}$$

Transfer approximately 0.200 gram of the nitric acid insoluble residue to a tared platinum crucible and weigh to the nearest 0.1 milligram. Determine the per cent boron in the residue by the procedure described above.

Calculate the per cent carbon from the per cent nitric acid insoluble and the per cent nitric acid insoluble boron as follows:

$$\frac{(\% \text{ Insol.} - \% \text{ Insol. B})(\% \text{ Insol.})}{100} = \% \text{ C}$$

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D. Determination of Boron in T-8 Caustic Scrubber Solutions Using Perchlorate Oxidation

General Discussion

T-8 caustic scrubber solutions (polymer destruction liquors) contain a considerable amount of boron in a form unsuitable for direct titration. This method is based on the conversion of all boron to soluble boric acid by heating with nitric and perchloric acids, followed by the standard mannitol-sodium hydroxide titration of the boric acid formed.

Apparatus

300 ml. Erlenmeyer flask with 24/40 $\frac{T}{S}$ joint
24/40 $\frac{T}{S}$ joint with 6-inch glass tube (inner member)
pH meter with glass and calomel electrodes

Reagents

70% perchloric acid, reagent grade
Concentrated nitric acid, reagent grade
Sodium hydroxide, 50% solution
Standard 0.1 N HCl
Standard 0.1 N NaOH
Mannitol, reagent grade

Procedure

Weigh a 40-50 gram sample into a 300 ml. Erlenmeyer flask with a $\frac{T}{S}$ 24/40 joint. Add 20 ml. of concentrated nitric acid and 25 ml. of 70% perchloric acid. Fit an inner member of 24/40 $\frac{T}{S}$ joint with 6 inches of tubing to act as an air condenser to the flask. Heat the flask at medium heat on a hot plate in the hood with a safety shield in front of the flask until all the nitric acid is decomposed or boiled off. Continue heating until the water has distilled off and perchloric acid begins refluxing in the walls of the flask. Reduce the heat and allow the perchloric acid to reflux for 20 minutes. Close the glass door of the hood. Increase the heat and bring to dense perchloric acid fumes. Continue the heating for 5 minutes. CAUTION: DO NOT HEAT LONGER THAN FIVE MINUTES. HOT, CONCENTRATED ACID CAN CAUSE VIOLENT EXPLOSIONS! Remove from heat, cool, and add 50 ml. of distilled water. Transfer contents of flask to a 400 ml. or 600 ml. beaker. Add 50% sodium hydroxide until basic. Add 0.1 N hydrochloric acid until neutral and then add 5 ml. in excess. Boil for 2 minutes to remove carbon dioxide. Cool. Add 0.1 N NaOH until a pH of 6.0 is reached. Add 10 grams of mannitol. Titrate with 0.1 N NaOH to a pH of 8.0. Record the ml. of 0.1 N NaOH required for the titration. Run a blank determination with the reagents. Subtract the blank value from the ml. of 0.1 N NaOH used in the determination to obtain the net titration for boron.

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Calculation

$$\% \text{ boron} = \frac{\text{ml. NaOH} \times \text{normality of NaOH} \times 1.082}{\text{sample weight in grams}}$$

Remarks

The above procedure is not necessary for T-10 scrubber (final destructive scrubber) solutions. They can be analyzed using the procedure for boron in soluble borates (C-2).

If a pH meter is not available, methyl red can be used to achieve a pH of 6.0 (orange color), and phenolphthalein can be used to determine when a pH of 8.0 (pink color) is reached.

E. Determination of Trimethylborate in Tetrahydrofuran

General Discussion

Trimethylborate may be determined by any one of three procedures: specific gravity, refractive index, and hydrolysis of the trimethylborate to boric acid and methanol with titration neutralization of the acidity from the boric acid-mannitol complex.



Apparatus

Standard Refractometer
Hydrometer, Sp. Gr. 0.880 to 0.950 scale

Reagents

0.10 N HCl
0.10 N NaOH
Methyl red indicator solution, 0.02% aqueous solution
Phenolphthalein indicator solution, 1% in 75% ethanol

Procedure

1. Specific Gravity

Specific gravity is determined by the normal procedure. It is necessary, however, to prepare a set of standards covering the possible range of percentage compositions to be found during operation, determining the specific gravity at a specified temperature and plotting a graph of specific gravity versus percentage trimethylborate. Samples to be determined are run under

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the same conditions, the specific gravity recorded and the percentage trimethylborate read directly from the graph prepared.

2. Refractive Index

The refractive index measurement is made in the usual manner. Standards prepared for the specific gravity determination may also be used to prepare a standard refractive index versus concentration of TMB curve. Samples received for analysis are run, the refractive index recorded and converted to percentage trimethylborate from either the standard curve or tables which may be prepared.

3. Hydrolysis and Titration

Pipette a one ml. sample into a 250 ml. Erlenmeyer flask containing 50-75 ml. of water, swirl gently and allow to stand for 5 minutes. Determine the boron present as outlined in "Determination of Boron in Soluble Borates."

Calculations

$$\frac{(\text{ml. HCl})(N \text{ HCl}) 10.38}{\text{ml. sample} \times \text{Sp. Gr.}} = \% \text{ Trimethylborate}$$

F. Determination of Free Chlorine and Silicon in Boron Trichloride

General Discussion

A liquid sample of boron trichloride is distilled into methanol. Addition of water hydrolyzes the methyl borate to boric acid and silicon to silicic acid. An aliquot of the resulting solution is analyzed for chlorine by the o-tolidine colorimetric method. Silicon in the residue from the distillation is determined colorimetrically by either the silico-molybdate method (over 25 ppm silicon) or the molybdenum blue method (below 25 ppm silicon). An aliquot of the methanol-water solution is also analyzed for silicon by either of the above two colorimetric methods. Total silicon is calculated by adding the amount of silicon determined in the distillate to that found in the residue.

Apparatus

The boron trichloride distillation apparatus consists of a modified Turner type absorption bulb fitted with a ball joint at the inlet tube, a small test tube to hold the sample, a right angle connecting tube, and appropriate clamps to support and join together the various parts of the apparatus.

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Sampling, Distillation and Absorption Procedure

Obtain a 1-3 ml. liquid boron trichloride sample by means of liquid transfer from the cylinder or reactor sample outlet into the sample tube which is chilled by a dry ice-acetone bath. Stopper the sample tube and keep it in a dry ice-acetone bath until ready for analysis. Place 25 ml. of absolute methanol (traces of moisture are not objectionable in the methanol) in the absorption bulb and weigh to the nearest 0.001 gram with the bulb in the closed position. Support the bulb securely about 12 inches above the bench top in the fume hood and attach the connection tube. Surround the absorption bulb with an ice water bath to slightly above the level of the methanol in the bulb. Withdraw the sample tube from the dry ice-acetone bath and quickly attach it to the connecting tube. Set the absorption bulb in the open position and allow the sample to distill over into the methanol. After all the sample has been distilled over (30-60 min.), close the absorption bulb inlet and detach the connecting tube. Dry the outside of the absorption bulb, open it momentarily to equalize pressure, and weigh the bulb to the nearest 0.001 gram. The difference in the bulb weights is the weight of the sample. The sample tube is stoppered and reserved for silicon analysis. Cold distilled water is run into the absorption bulb. The mixture in the absorption bulb is washed into a 100 ml. volumetric flask and made up to volume with distilled water.

Chlorine Analysis

1. Reagents

a. O-Tolidine

Dissolve 0.186 gram of o-tolidine (Eastman No. 249) in solution containing 37 ml. of concentrated hydrochloric acid and 75 ml. of distilled water. Dilute to 250 ml. with distilled water and store in dark brown bottle.

b. Standard Potassium Chlorate Stock Solution (1.000 g/l)

Dissolve 1.000 gram of reagent grade $KClO_3$ in distilled water and dilute to 1.000 liter with distilled water.

c. Standard Potassium Chlorate Solution (0.0500 g/l)

Pipette out 50.00 ml. of standard potassium chlorate stock solution into a one liter volumetric flask and dilute to the mark with distilled water. This solution contains 0.01446 gram of chlorine per liter.

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2. Preparation of Calibration Curve

In a series of five 250-ml. glass-stoppered Erlenmeyer flasks place portions of standard potassium chlorate solution (0.0500 gm. KClO_3 per liter) ranging from 0.0 to 4.0 ml. in steps of 1.0 ml. Dilute the contents of each flask to 40 ml. with distilled water and add 40 ml. of 1:1 HCl to each. Warm each flask to 40°C and hold at this temperature for 30 minutes. Cool, transfer each solution to a 100 ml. volumetric flask. Add 2 ml. of o-tolidine reagent to each volumetric flask and dilute to the mark with distilled water. Shake well. Using the solution containing no potassium chlorate in the reference cell, read the absorbancy of each solution at 438 millimicrons on the Beckman DU Spectrophotometer approximately 9 minutes after color development. Plot a standard curve of absorbancy as a function of micrograms of chlorine.

3. Procedure for Chlorine Determination

From the solution containing the washings from the boron tri-chloride absorption bulb, pipette a suitable aliquot into a 100 ml. volumetric flask. Use 20 of the 100 ml. if in doubt. Dilute to 40 ml. with distilled water. Add 40 ml. of 1:1 hydrochloric acid. In a separate 100 ml. volumetric flask prepare a blank by adding 40 ml. of 1:1 hydrochloric acid to 40 ml. of distilled water. Add 2.0 ml. of o-tolidine reagent to each flask, dilute to the mark with distilled water and mix well. Read the absorbancy at 438 m μ of the unknown solution nine minutes after color development with the blank in the reference cell. Determine micrograms of Cl in the unknown solution by referring to the calibration curve.

Calculation

$$\text{ppm Cl in sample} = \frac{\text{micrograms Cl in solution (100)}}{\text{ml. aliquot for Cl analysis (sample wt. in gms.)}}$$

Silicon Analysis - Silicomolybdic Acid Method (over 25 ppm Si)

1. Reagents

a. Standard Silicon Solution (0.1000 gm. Si per liter)

Ignite reagent grade silica at 1000-1100°C in a platinum crucible to constant weight. Weigh out 0.2140 gm. of the ignited silica into a platinum crucible. Add approximately 2 gms. anhydrous reagent grade sodium carbonate and mix intimately with a well-rounded, thin, dry glass rod. Cover the crucible and gradually heat the mixture to fusion. Maintain it slightly above fusion temperature for 15 minutes. Cool, and place the crucible and cover in a polyethylene beaker. Dissolve the melt in warm

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water. When solution is complete, remove the crucible and cover from the beaker, washing them thoroughly with a stream of distilled water, combining the solution and washings. Cool the solution to room temperature, and transfer to a liter volumetric flask. Dilute to volume and mix thoroughly. Transfer the solution to polyethylene bottles for storage. The solution contains 0.1 mg. silicon per milliliter (100 ppm Si).

b. Glacial Acetic Acid, Reagent Grade

c. Ammonium Molybdate, 5% Aqueous Solution

d. 2, 4-dinitrophenol Indicator Solution, 0.1%
Aqueous Solution, Eastman No. A 102

2. Preparation of Calibration Curve

To a series of 100 ml. volumetric flasks, pipette in 0.0 to 6.0 ml. of standard silicon solution in steps of 0.1 ml. Dilute each to approximately 50 ml. Add 1.0 ml. of 2,4-dinitrophenol indicator. Add 1.0 ml. of glacial acetic acid and 5.00 ml. of 5% aqueous ammonium molybdate solution. Dilute each flask to the mark with distilled water and mix thoroughly. Allow solutions to stand 5 to 10 minutes. Read the absorbancy of each solution at 420 millimicrons using the blank in the reference cell of the DU Spectrophotometer. Prepare the calibration curve by plotting absorbancy at 420 millimicrons versus mg. of silicon per 100 ml. of solution.

3. Procedure for Analysis of Silicon in Boron Trichloride

Pipette an aliquot of the solution prepared from the washings from the boron trichloride absorption bulb (0.1-0.4 mg. of Si) into a 100 ml. volumetric flask and dilute to approximately 50 ml. Use a separate 100 ml. volumetric flask for a reagent blank. Add one ml. of 2,4-dinitrophenol indicator. Add concentrated ammonium hydroxide dropwise, while swirling, until the solution assumes a yellow color. Wash down the neck of the flask with a stream of distilled water and add 1:1 hydrochloric acid dropwise until the yellow color is just discharged. Add one ml. of glacial acetic acid and 5.00 ml. of 5% ammonium molybdate solution. Dilute to volume and mix thoroughly. After 15 minutes read the absorbancy of the solution on a Beckman DU Spectrophotometer at 420 millimicrons with the reagent blank set at zero absorbancy. Convert the absorbancy reading to milligrams of silicon by means of the calibration curve. Label this value Y.

Wash the residue in the sample tube from the boron trichloride distillation into a 100 ml. volumetric flask with water and determine the milligrams of silicon in the residue by the above procedure.

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Calculations

Total mg. Si in sample = mg. Si in residue + $\frac{Y (100)}{\text{aliquot of absorption bulb solution}}$

% Si = $\frac{\text{Total mg. Si Y in sample}}{\text{grams sample (10)}}$

Silicon Analysis - Molybdenum Blue Method (under 25 ppm Si)

1. Reagents

a. Standard Silicon Solution, 0.01 mg. Si per ml.

Prepare a solution containing 0.1 mg. Si per ml. using the directions outlined in the preceding silico molybdic acid method. Adjust the final dilution of the standard so that one ml. of the solution contains 0.01 mg. silicon.

b. Stannous Chloride Solution

Transfer 1.0 gm. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystals to a 100 ml. volumetric flask. Dissolve in 2 ml. of concentrated hydrochloric acid, added by means of a pipette. Dilute to the mark with distilled water. Prepare a fresh solution every one or two days.

Ammonium molybdate, 5% aqueous solution.

2. Preparation of Calibration Curve

Pipette 0, 1, 2, 3 and 5 ml. of the silicon standard solution (0.01 mg. Si per ml.) into separate 100 ml. volumetric flasks. Dilute each to approximately 50 ml. with distilled water. Add one ml. of 1:3 sulfuric acid, followed by 10 ml. of 5% ammonium molybdate reagent. Mix and allow to stand 5 minutes, then add 30 ml. of 1:3 sulfuric acid. Mix thoroughly, rinse neck of flask with small amount of distilled water and mix again, then add 1.0 ml. of stannous chloride reagent and mix immediately. Dilute to the mark, mix thoroughly and allow to stand at least 20 to 25 minutes. Read the absorbancy at 815 millimicrons on the DU Spectrophotometer using 1 cm. cored cell, the reagent blank being set at zero absorbancy. Plot absorbancy reading versus micrograms of silicon per 100 ml. to obtain calibration curve.

3. Procedure for Determination of Silicon in Boron Trichloride

Pipette an aliquot of the solution prepared from the washings from the boron trichloride absorption bulb (0.01-0.04 mg. of Si) into a 130 ml.

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polyethylene bottle which has previously been calibrated at 100 ml. Dilute to about 30 ml. with distilled water. Add one ml. of 2,4-dinitrophenol indicator. Run in concentrated ammonia solution carefully from a graduated 10 ml. pipette with constant swirling until the solution turns yellow. Note the volume of ammonia used and add the same amount to the reagent blank. Now, add concentrated hydrochloric acid carefully to the sample and blank by means of a dropper, while swirling, until the yellow color has just been discharged, then add one ml. of 1:3 sulfuric acid, and 10 ml. of 5% ammonium molybdate. Mix and allow to stand 5 minutes; add 30 ml. of 1:3 sulfuric acid, wash neck of bottle with distilled water, mix well, and add 1.0 ml. of stannous chloride. Dilute to the 100 ml. mark and allow to stand for at least 20-25 minutes. Read the absorbancy of the solution at 815 millimicrons as in the procedure for the calibration curve with the reagent blank set at zero absorbancy. Convert the absorbancy reading to micrograms of silicon by means of the calibration curve. Label micrograms of silicon Q.

Wash the residue in the sample tube from the boron trichloride distillation into a 130 ml. polyethylene bottle which has previously been calibrated at 100 ml. with water and determine the micrograms of silicon in the residue by the above molybdenum blue procedure.

Calculations

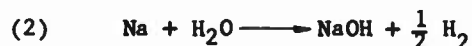
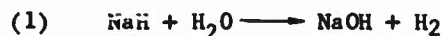
Total mg. of Si in sample = mg. Si in residue + $\frac{Q (100)}{\text{aliquot of absorption bulb soln.}}$

ppm Si = $\frac{\text{total micrograms of Si in sample}}{\text{sample weight in grams}}$

G. Analysis of Sodium Hydride

General Discussion

This method is based on the decomposition of sodium hydride (NaH) and free sodium (Na) by isopropanol and water, according to the equations:



The volume of hydrogen evolved is determined by means of a gas burette. The reaction mixture is then titrated for total alkalinity, and the per cent of sodium hydride and sodium calculated from the volume of hydrogen and the alkalinity with the aid of Equations (1) and (2). In the absence of free sodium, the per cent of sodium hydride is calculated from the volume of hydrogen alone, based on Equation (1), or from the alkalinity.

The method is applicable to NaH-solids and their dispersions in high-boiling, inert, organic media, such as mineral oils.

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Solvents possessing high vapor pressures interfere with the determination of the true hydrogen volume and should be removed, if possible. Titratable alkalinity other than that derived from NaH and Na also interferes.

The accuracy of the method is within $\pm 1\%$ of the amount of each constituent (NaH, Na) present.

The precision is governed by the homogeneity of the NaH-Na mixtures.

Safety Aspects

Sodium hydride reacts very vigorously with water and may ignite spontaneously. Proper care should therefore be exercised in the handling of this material. Any NaH (or slurry) adhering to spatulas or glass droppers should be destroyed by first rinsing with isopropanol or methanol.

Special Apparatus and Reagents

1. Special Apparatus

The apparatus consists of:

a. A 100 ml. Fisher gas burette (Fisher Catalog No. 10-600-36), jacketed by a wide glass tube (13" x 2"), modified for greater capacity, as follows:

The glass stopcock at the top of the burette is cut off. The free end (capillary tube) is connected to the bottom stopcock of a gas sampling tube of 250 ml. capacity (Central Scientific Co. Cat. No. 20810) by means of a piece of pure gum rubber tubing. The lower end of the gas burette is connected to a piece of glass tubing (about 100 cm. in length, 6 mm. dia.) and to a leveling bulb of one liter capacity via a T-tube and rubber tubing. The glass tube is clamped up in a vertical position alongside the gas burette and serves as a convenient gauge for reading the water level in the burette. An extra stand and ring clamp are provided for the leveling bulb.

b. A gas-evolution vessel. This consists of a 125 ml. Pyrex filtering flask, provided with a rubber stopper, through which passes the stem of a small separatory funnel (60 ml. capacity, cylindrical type). The side outlet of the gas-evolution flask is connected to the top of the gas sampling tube by means of a long piece of rubber tubing.

c. A thermometer, (suspended next to the gas burette), for recording the room temperature (0-100°C).

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2. Special Reagents

Isopropanol (technical grade)
Hydrochloric Acid, approximately 0.5 N
Methyl Red Indicator, 0.02% aqueous soln.

Procedure

1. Calibration of Modified Gas Burette

Disconnect the T-tube at the bottom of the burette and replace it by a piece of short rubber tubing, provided with a pinch clamp. Completely fill burette and gas sampling tube with distilled water, introduced at the bottom (pinch clamp open). The water should extend a short distance past the capillary tube of the upper stopcock of gas sampling tube. Close pinch clamp and place an arbitrary calibration-mark at the upper level of the water. Now, open the pinch clamp and run out the water from the upper reservoir (gas sampling tube) into a large beaker. Stop after the water level has reached a calibrated part of the gas burette (at 96 ml., say). Measure the volume of water collected between these two calibration points, using volumetric flasks and graduates. Repeat the calibration 2 or 3 times and obtain an average value.

2. Determination

a. Gas Analysis

Completely fill the gas burette and calibrated reservoir with distilled water, introduced via the leveling bulb, then fill the bulb itself with distilled water up to approximately 1/3 of its volume. Remove any air bubbles by squeezing the rubber tube connecting the bulb to the burette. Carefully raise the leveling bulb until the water level reaches the top calibration mark of the reservoir (gas sampling tube) and support bulb in ring clamp at this point.

Weigh accurately about 290-320 mg. of the solid or 1.00-1.20 gms. of the dispersion (Note 1) into the gas-evolution flask (Note 2). Connect gas-evolution flask to burette and tightly insert rubber stopper with separatory funnel into neck of flask. Close stopcock of funnel, then lower the leveling bulb as far as possible and fix with clamp. Place 10 ml. of isopropanol into separatory funnel, immerse flask in a cooling bath (tap water) and gradually add the alcohol to sample, leaving a small amount of it in funnel, as a seal. Now, slowly add 20 ml. of distilled water (Note 3), leaving a water seal in funnel. Remove flask from cooling bath and allow the system to come to equilibrium (Note 4). Raise leveling bulb, until the water level (in gauging tube) coincides with that in the burette. Read the burette at this point and record as the final water volume. Also record the room temperature and barometric pressure. Disconnect gas-evolution flask and retain the reaction for titration.

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b. Titration

Add 6-8 drops of methyl red indicator to the above solution and titrate to neutrality with approximately 0.5 N HCl. Record milliliters of HCl used.

Calculations

1. Both NaH and Na Present

Calculate results as follows:

Volume of hydrogen gas (ml.) at standard temperature + pressure = H_2V_{STP} , then

$$V_{STP} = V \times \frac{P}{760} \times \frac{273}{T}$$

V_1 = Total volume of gas burette, ml. (by calibration)

V_2 = Final water volume, ml. (after reaction)

V_3 = Vol. of isopropanol + vol. H_2O added, ml. (= 30 ml.)

v = Volume of hydrogen gas, ml. uncorrected, = $(V_1 - V_2) - V_3$

P_0 = Barometric pressure, mm. Hg.

P_1 = Vapor pressure of 1:2 mixture of isopropanol + H_2O
(= 34.0 mm. Hg., as determined in laboratory at 23°C)

P = $P_0 - P_1$, mm. Hg.

T = $273 + t^\circ$, °K

t° = Room temperature, °C

A = Total milliequivalents of NaOH = ml. HCl x normality of HCl

Then,

$$\frac{\left(\frac{H_2(V_{STP}) \times 2}{22.4} - A \right) \times 24}{\text{sample weight} \times 10} = \% \text{ NaH}$$

$$\frac{\left(A - \frac{H_2(V_{STP})}{22.4} \right) \times 46}{\text{sample weight} \times 10} = \% \text{ Na,}$$

where H_2V_{STP} = ml. H_2 at standard temperature and pressure. Sample weight in milligrams.

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2. Na Absent

If the formula for % Na should result in values 0, Na is absent and the per cent of NaH is calculated as follows:

a. From Volume of Hydrogen

$$\frac{H_2(V_{STP}) \times 100}{\text{sample weight} \times 933.3} = \% \text{ NaH}$$

(933.3 = ml. H_2 per gm. of 100% NaH, theoretical)

b. From HCl - Titration

$$\frac{\text{ml. HCl} \times N \text{ of HCl} \times 0.024 \times 100}{\text{sample weight}} = \% \text{ NaH}$$

Notes:

1. The sample weights used for NaH solids and dispersions depend on the ratio of NaH:Na (and on the concentration of the dispersions). The more Na is present, the less the volume of hydrogen evolved. In general, the sample weights have to be selected in such a manner that the volume of hydrogen produced does not exceed the capacity of the modified gas burette (ca. 300-350 ml.). This may require a preliminary trial.

2. The samples are best weighed directly into the gas-evolution flask, tared on the analytical balance. In order to exclude moisture as much as possible, the flask carries a rubber stopper, and a rubber cap is slipped over its side-outlet. (The whole system is weighed.)

All dispersions should be shaken vigorously before weighing, in order to obtain a uniform sample. The transfer of the dispersion-sample to the tared flask is effected by means of a dropper. All weighings should be performed as rapidly as possible.

3. Addition of water to the isopropanol-NaH mixture immediately results in a very vigorous evolution of hydrogen. It is therefore of importance to add only a very small portion of water at the start, by momentarily opening and closing the stopcock of the separatory funnel. After the first, vigorous reaction has subsided; this procedure is repeated until most of the NaH has reacted. The remainder of the water may then be run in more rapidly.

4. The system has reached equilibrium (after gas-evolution), if the water level in the gas burette remains constant. The attainment of equilibrium may be hastened by gently swirling the gas-evolution flask and noting any depression in the water level of the burette.

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H. Analysis of NaOCH₃ in Filtrate from Sodium Borohydride Recovery

General Discussion

Sodium methylate is determined by hydrolysis to convert the NaOCH₃ to NaOH and CH₃OH, followed by titration with standard acid to determine the alkalinity produced.

Reagents

Standard 0.1 N hydrochloric acid
Methyl red indicator

Procedure

Pipette from 1 to 5 ml. of sample into a 250 ml. Erlenmeyer flask containing 50 ml. of water. Swirl the flask gently until all hydrolysis reaction has ceased. Add 6 drops of methyl red and titrate to the neutral point with standard N/10 hydrochloric acid, record the amount of standard acid required.

Calculations

$$\frac{(\text{ml. HCl})(N \text{ HCl})}{\text{ml. sample}} \frac{54.02}{1} = \text{grams/liter NaOCH}_3$$

I. Determination of Mineral Oil in Sodium Borohydride Process Materials

General Discussion

This method is based on the extraction of mineral oil with dichloromethane from an acidified aqueous solution of the sample. The dichloromethane is evaporated and the mineral oil residue is dried and weighed.

This method can be used to determine the mineral oil content of samples of sodium borohydride, sodium fluoride, sodium chloride, and solutions of these materials in methyl borate, tetrahydrofuran, anisole, ether, and water.

Any material that is extractable with dichloromethane and will not evaporate below 110°C will interfere with this method.

The accuracy (recovery) of this method is $\pm 0.5\%$ of the amount present.

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Safety Aspects

The usual safety precautions with respect to sodium borohydride, strong acids, and organic solvents should be observed. There is a fire hazard due to the hydrogen evolved from sodium borohydride and its solutions. Use adequate ventilation when handling the dichloromethane.

Reagents

1. Hydrochloric acid solution, 1:1. One volume C.P. hydrochloric acid to one volume distilled water.
2. Dichloromethane, b.p. 40-42°C from Matheson, Coleman and Bell, or equivalent.
3. Ethyl alcohol (anhydrous)

Procedure

Weigh a sample containing 5 to 500 mg. of mineral oil to the nearest 0.1 mg. and transfer by washing with distilled water into a 250 ml. Erlenmeyer flask. Add distilled water to bring the volume up to 100 ml., acidify with 50% hydrochloric acid solution and transfer the acidified solution to a 250 ml. separatory funnel. Do not use any grease on the stopcock. Rinse the flask with 50 ml. of distilled water and add to the separatory funnel. Add 10-15 ml. of dichloromethane to the flask, stopper with a clean rubber stopper, shake vigorously and transfer to the separatory funnel.

Stopper the separatory funnel and shake it for one minute to extract the mineral oil. Allow the solution to clearly separate into two phases and transfer the organic phase to a second separatory funnel. Wash with 150 ml. of distilled water acidified with 3 ml. of 50% hydrochloric acid solution and transfer the organic phase to a tared, clean dry 50 ml. beaker. Place a second portion of dichloromethane in the Erlenmeyer flask and run it through the above extraction procedures with the same aqueous wash solution and combine it with the first portion in the beaker. Repeat with a third portion of dichloromethane.

Place the beaker on a steam bath and evaporate the solvent down to 2-3 ml. Add one ml. of ethyl alcohol and evaporate the solvents. Place the beaker in an oven at 110°C for one hour to complete the evaporation, cool, and weigh to the nearest 0.1 mg. Obtain the weight of mineral oil by difference.

Calculations

$$\frac{\text{net gms. of mineral oil}}{\text{gms. of sample}} \times 100 = \% \text{ mineral oil}$$

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J. Determination of Methoxy Groups in Sodium Borohydride Process Materials

General Discussion

This method is based on the hydrolysis of the methoxy groups to methanol, distillation of the methanol, and titration of methanol in the distillate with a standardized ceric nitrate solution.

This method can be used on sodium chloride and sodium fluoride salts, borohydride, fluoborates, and solutions of these materials in water or methyl borate.

Any material which will distill over with the methanol and which will be oxidized by the ceric solution will interfere with this method. Tetrahydrofuran is a material of this type.

The accuracy (recovery) of this method is $\pm 0.5\%$ of the amount present.

Safety Aspects

The usual safety precautions with respect to sodium borohydride, osmium tetroxide, arsenic salts, and strong acids should be observed. There is a fire hazard due to the hydrogen evolved from sodium borohydride and its solutions.

Reagents

1. Phosphoric acid solution. One part 85% reagent grade phosphoric acid to 3 parts distilled water.
2. Nitric acid. Boiled reagent grade nitric acid.
3. Arsenious oxide solution, 0.1000 N. Dissolve 2.4725 gms. of pure Bureau of Standards arsenious oxide in 20 ml. of 1 N sodium hydroxide. Add sufficient 1 N sulfuric acid to make the solution slightly acid to litmus. Dilute the solution to 500 ml.
4. Ceric ammonium nitrate, 0.1 N. Dissolve approximately 60 gms. of ceric ammonium nitrate (G. Frederick Smith, reagent) to 500 ml. of distilled water containing 90 ml. of boiled concentrated nitric acid. Dilute the solution to 1000 ml. Standardize this reagent against the standard arsenite solution.
5. Osmium tetroxide, 0.01 N. Dissolve 0.5 gm. of osmium tetroxide, reagent grade, in distilled water and dilute to 200 ml.

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6. Sulfuric acid solution, 6 N.
7. Ferroin indicator. 1,10 (ortho)-Phenanthroline Ferrous Sulfate, G. Frederick Smith, reagent.

Procedure

1. Distillation

Weigh a sample containing approximately 25 mg. of methoxy groups to the nearest 0.1 mg. and transfer to a 300 ml. Kjeldahl flask. Use 125-130 ml. of distilled water to aid the transfer and to wash down the neck of the flask. Add two boiling stones and connect the flask to a Kjeldahl type distillation apparatus equipped with a dropping funnel and a 500 ml. $\frac{1}{2}$ flask as a receiver. Add 10 ml. of phosphoric acid solution dropwise through the dropping funnel and follow with 3 ml. of distilled water. When the vigorous reaction subsides, heat the Kjeldahl flask slowly until smooth boiling is obtained. Continue the distillation until about 100 ml. of distillate are collected in the receiving flask. The distillation flask must not be allowed to run dry.

2. Titration

Add to the distillate 10 ml. of nitric acid and 50.00 ml. of the ceric ammonium nitrate solution which has been filtered through a Gooch crucible under slight suction just prior to use. Place the flask with the distillate under a vertical $\frac{1}{2}$ reflux condenser, reflux for 10-12 minutes and cool.* Wash the reflux condenser with 10 ml. of distilled water and combine the wash with the distillate. Add 20 ml. of sulfuric acid, eight drops of osmium tetroxide solution (as a catalyst), two drops of ferroin indicator, and swirl to insure complete mixing. Titrate the excess ceric ion with 0.1 N arsenious oxide solution to the first permanent pink color. Exercise caution when approaching the endpoint. The endpoint is a rapid change from yellow to pink but there is sometimes a delay in the reduction of the ceric ion by the arsenite ion.

Record the volume of ceric solution used up as the uncorrected methoxy titration. Run a blank, containing the reagents and solvents used in the sample, and correct the sample titration for the blank.

Calculations

$$\% \text{OCH}_3 = \frac{(\text{net ml. of ceric soln.})(N \text{ of ceric soln})(7.758)}{\text{grams of sample (10)}}$$

$$7.758 = \frac{\text{mol. wt. of OCH}_3}{4} = \frac{31.034}{4}$$

*Observe the distillate closely during the initial refluxing. If the distillate becomes colorless, due to the complete reduction of the ceric ion, quickly add an additional aliquot of the ceric ammonium nitrate solution through the top of the condenser.

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II. Infrared Methods

A. Infrared Determination of Boron Trichloride in Gas Samples

General Discussion

This method is based on the infrared absorption of boron trichloride at 5.22 or 11.06 microns. A calibration curve is prepared by measuring the absorbance of samples containing known pressures of boron trichloride and samples are analyzed by reference to the calibration curve.

Apparatus

Beckman IR-4 infrared spectrophotometer
100 mm. gas cell

Reagents

Boron trichloride

Procedure

Preparation of Calibration Curve

The gas is handled by means of standard high vacuum techniques. Boron trichloride is transferred to the cell at various pressures from 0 to 200 mm. of mercury and scanned from 15 to 2 microns at suitable instrument conditions. The absorbances at the two wavelengths are obtained using the base line method of analysis and are used to prepare the calibration curves.

Estimation of Boron Trichloride

A sample of the gas to be analyzed is introduced into the infrared cell at known pressure sufficient to give a partial pressure of boron trichloride in the range of the calibration curve. The sample is scanned under the same instrumental conditions as used in preparing the calibration curve and the absorbance is calculated using the base line technique. The partial pressure of boron trichloride is obtained from the calibration curve and the mole per cent is calculated from the equation:

$$\text{Mole \% BCl}_3 = \frac{\text{partial pressure of BCl}_3 \times 100}{\text{total cell pressure}}$$

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B. Infrared Determination of Phosgene

General Discussion

The method is based on the infrared absorption of phosgene (COCl_2) at 5.42 or 11.77 microns. A calibration curve is prepared by measuring the absorbances of samples containing known partial pressures of phosgene in a 100 mm. infrared gas cell.

Apparatus

Beckman IR-4 Infrared Spectrophotometer
100 mm. gas cell

Reagents

Phosgene (The Matheson Co., Inc.)

Procedure

Preparation of Calibration Curve

Phosgene is handled by means of standard high vacuum techniques. Phosgene at various pressures from 0-7 mm. of mercury is transferred to the cell and scanned from 15 to 2 microns using one micron per minute scanning speed, two times standard slit width, and 1.5 per cent gain. The absorbances at 5.42 and 11.77 microns are obtained using the base line technique of analysis and the absorbances obtained are used to prepare the calibration curve.

Estimation of Phosgene

A sample of the gas to be analyzed is introduced into the infrared cell at a pressure sufficient to give a partial pressure of phosgene within the range of the calibration curve. The sample is scanned under the same instrumental conditions are used in preparing the calibration curve and the absorbance is calculated using the base line technique. The partial pressure of phosgene is obtained from the calibration curve and the mole per cent phosgene is calculated from the equation:

$$\text{Mole \% phosgene} = \frac{\text{partial pressure of phosgene} \times 100}{\text{total pressure in cell}}$$

C. Infrared Determination of Methyl Chloride in Gas Streams

General Discussion

This method is based on the infrared absorption of methyl chloride at 13.67 microns. A calibration curve is prepared using known partial

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pressures of methyl chloride over the range of 0 to 30 mm. of mercury in a gas cell with a constant total gas pressure.

Estimation of the partial pressure of methyl chloride in a gas sample is made using this curve.

Apparatus

Beckman IR-4 Infrared Spectrophotometer
100 mm. gas cell

Reagents

Methyl chloride

Procedure

Preparation of Calibration Curve

All gases are handled by means of standard high vacuum techniques. Methyl chloride at various pressures from 0 to 30 mm. of mercury is transferred to the cell.

The standards are scanned from 15 to 10 microns using a 3% gain and two times standard slit width. The absorbance at 13.67 microns is obtained using the base line method of analysis, and the absorbances obtained for the standards are used to prepare the calibration curve.

The curve is a plot of absorbance as a function of mm. methyl chloride pressure.

Estimation of Methyl Chloride

A sample of gas containing unknown quantities of methyl chloride is transferred to the infrared gas cell at known pressure. The sample is scanned under the same instrumental conditions as used in preparing the calibration curve, and the absorbance at 13.67 microns is calculated using the base line technique. The partial pressure of methyl chloride is obtained from the curve. From the partial pressure of the methyl chloride and the total pressure of the gas in the infrared gas cell, the mole per cent methyl chloride in the sample is calculated.

Calculation

$$\text{Mole \% methyl chloride} = \frac{\text{partial pressure of methyl chloride} \times 100}{\text{total pressure of sample}}$$

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D. Infrared Determination of Ansul Ether E-141 in Mineral Oil

General Discussion

This method is based on the infrared absorption of Ansul Ether E-141 in mineral oil at 8.97 microns. A calibration curve is prepared using known concentrations, and estimation of the concentration of Ansul Ether E-141 is made using this curve.

Apparatus

Beckman IR-4 Infrared Spectrophotometer
0.0264 mm. cell

Reagents

Ansul Ether E-141, Ansul Chemical Co., Marinette, Wisc.
Mineral Oil, Bayol 85, Chevron NF No. 3, USP No. 15

Procedure

Preparation of Calibration Curve

Prepare standard solutions by dissolving known quantities of Ansul Ether E-141 in mineral oil. The concentration used is 0-15% Ansul Ether E-141 by weight. The absorption of each solution in a 0.0264 mm. cell is measured at 8.97 microns using a 0.50 mm. slit width, 0.629% gain and an 8 second period. The absorbances are obtained by using single beam point analysis. This consists of placing pure mineral oil in the infrared cell, placing the cell in the sample beam of the instrument and increasing the instrument gain until there is zero absorbance on the scale. The sample is then placed in the cell and absorbance is recorded.

Analysis

Unknown samples of Ansul Ether E-141 in mineral oil are analyzed by measuring the absorbance under the same conditions as used in preparing the calibration curve and obtaining the concentration by reference to the calibration curve.

E. Determination of Tetrahydrofuran in Mineral Oil

General Discussion

This method is based on the measurement of the absorption of tetrahydrofuran in mineral oil at 9.31 microns. A calibration curve is prepared with known concentrations of tetrahydrofuran and estimation of the unknown

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samples is made by use of this curve. A Beckman IR-4 infrared spectrophotometer was used for the analysis.

Preparation of Calibration Curve

Dissolve one milliliter of tetrahydrofuran in mineral oil (Bayol No. 85) and dilute to volume in a 100 ml. volumetric flask. This solution is one volume per cent tetrahydrofuran in mineral oil and is used to prepare other samples of known concentration by successive dilutions. Known samples are prepared in this manner containing 0.50, 0.30, 0.10 and 0.05 volume per cent THF. After thorough mixing, the absorbances of the known solutions in a 0.1 mm. cell are observed and the calibration curve prepared.

The absorbances are obtained by using single beam point analysis. This consists of filling the cell with pure mineral oil, placing the cell in the sample beam of the instrument and increasing the instrument gain until the absorbance reads zero. This sample in mineral oil is then placed in the cell and the absorbance observed and recorded.

Determination of Tetrahydrofuran

An unknown sample of tetrahydrofuran in mineral oil is analyzed by filling the infrared cell with the sample, measuring the absorbance under the same conditions as used in preparing the calibration curve and obtaining the concentration by reference to the calibration curve. The range of the analysis is 0.05 to 1.0% with accuracy of $\pm 0.01\%$.

F. Determination of Sodium Borohydride in Ansul Ether E-181

General Discussion

This method is based on the measurement of the infrared absorption of sodium borohydride in Ansul Ether E-181 at 4.48 microns. A calibration curve is prepared from the absorbances of known concentrations of sodium borohydride and estimation of unknown samples is made by use of the curve. A Beckman IR-4 infrared spectrophotometer was used for this analysis.

Preparation of Calibration Curve

Prepare known concentrations of Metal Hydrides Company's sodium borohydride in Ansul Ether E-181 ranging from 0.01 g./100 ml. to 8.0 g./100 ml. Scan each sample between 6.0 and 2.0 microns in a 0.03 mm. cell. Calculate the absorbance of each sample by the base line method of analysis, then prepare a calibration curve from the data obtained.

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The base line method of analysis is explained in most texts on instrumental analysis and is not discussed here.

Determination of Sodium Borohydride

To analyze for sodium borohydride in Ansul Ether E-181, fill a 0.03 mm. cell and scan the sample between 6 and 2 microns with the same instrumental settings as used in preparing the calibration curve. The absorbance of the sample is then calculated and the concentration obtained from the calibration curve.

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APPENDIX C

Physical Properties of Boron Trichloride

(These graphs illustrate the conflicting data
on liquid boron trichloride as reported in
various literature sources.)

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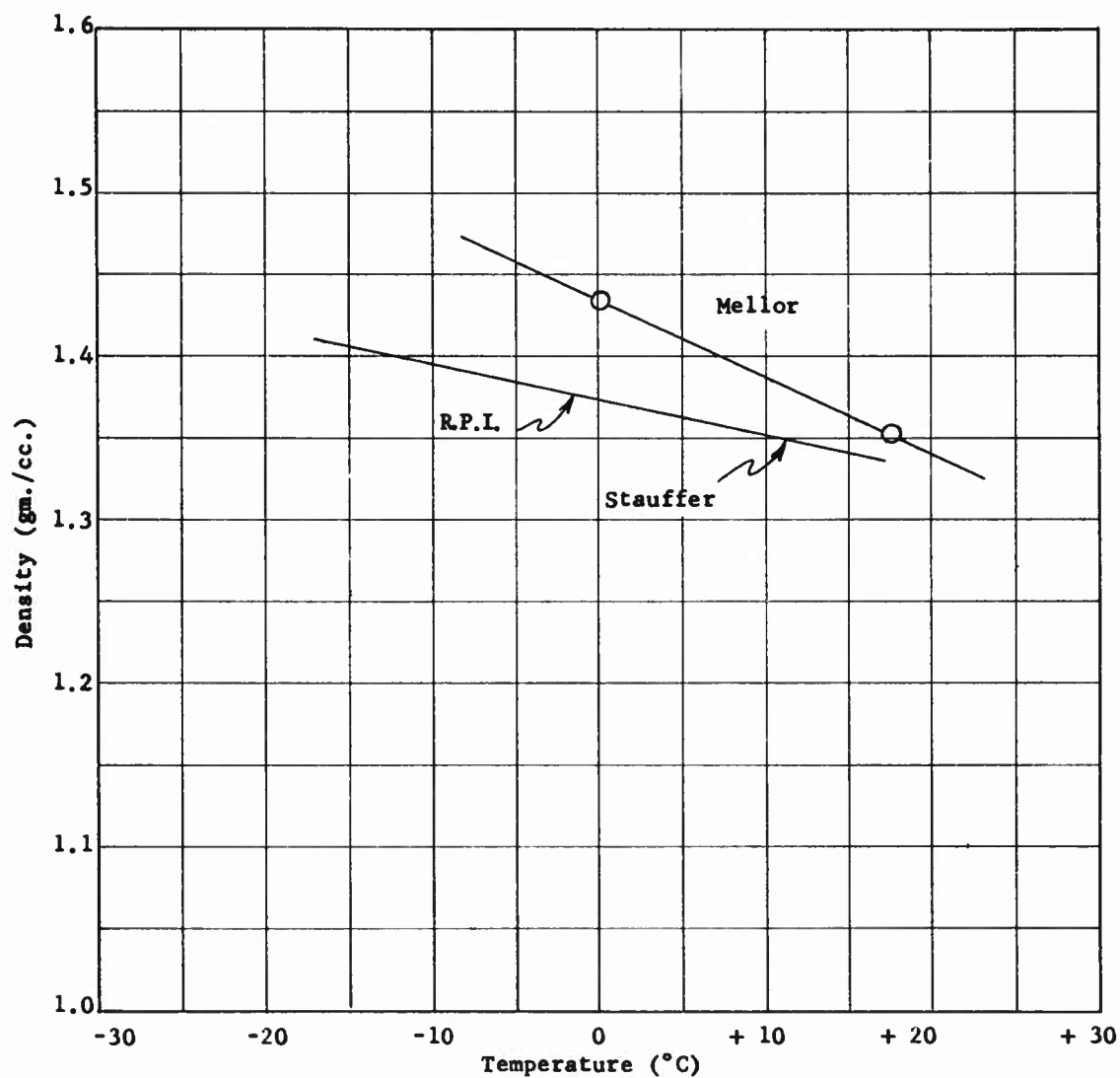


Figure C-1. Density of Liquid BCl₃

C-1

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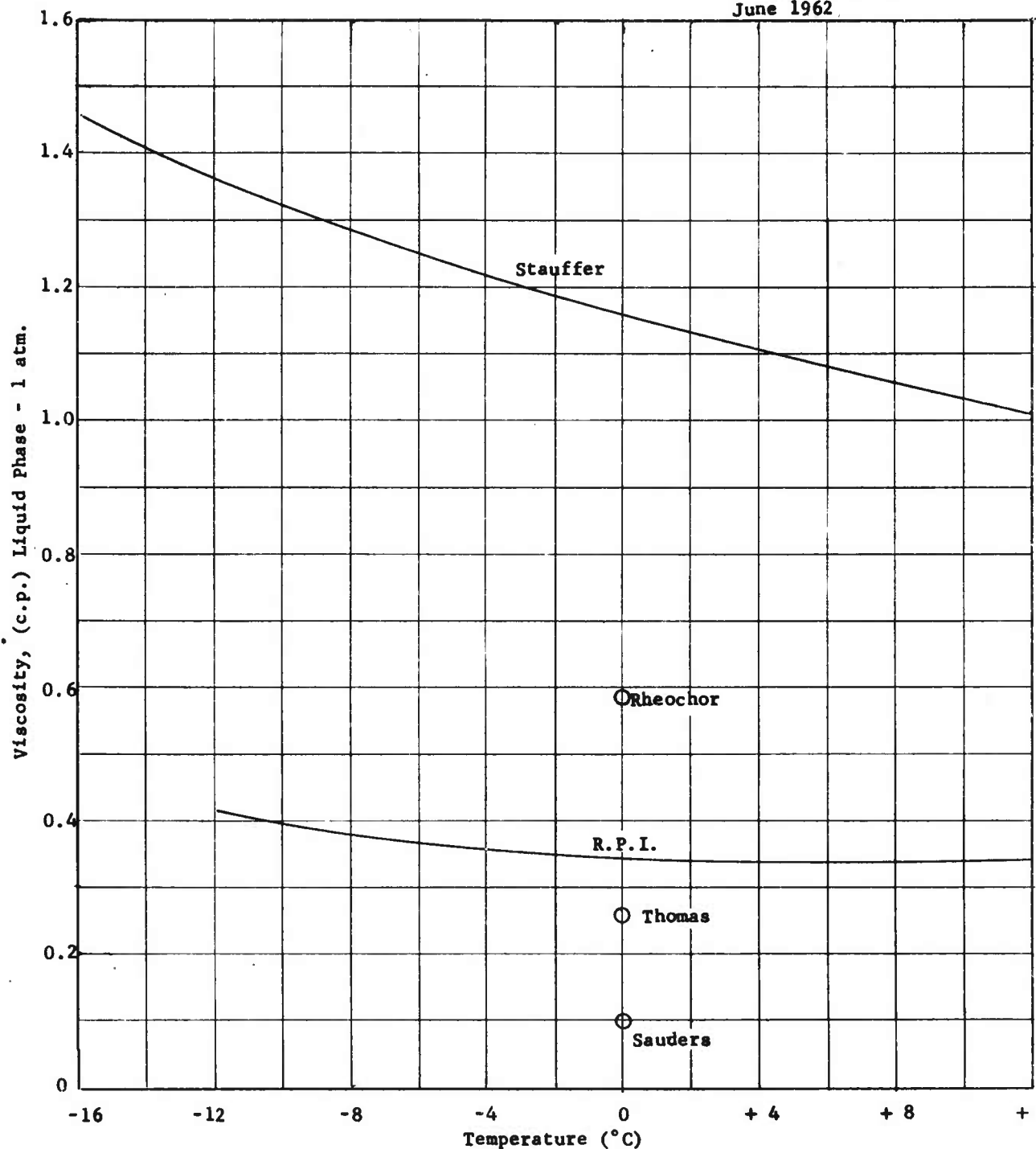


Figure C-2. Viscosity of BCl₃ as a Function of Temperature

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APPENDIX D

Boiling Points of Boron Compounds

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APPENDIX D

Boiling Points of Boron Compounds (see Figure D-1)

	<u>Compound</u> <u>B_nH_m</u>	<u>B.P. (°C)</u>	<u>P</u>	<u>Reference</u>
(1)	B ₂ H ₆	-92.5	121.9 - expt'l value, std. (B=9.55)	(b)
(2)	B ₄ H ₁₀	17.8	209.2	(b)
(3)	B ₅ H ₁₁	65	235.9	(b)
(4)	B ₁₀ H ₁₄	213	335	(b)
(5)	B H ₃	-170	60.8 est. by plot for B _n H _m	(-)

BR₃ (see also (5), above) used as cross check

(6)	B(CH ₃) ₃	-20	177.85	(a)
(7)	B(C ₂ H ₅) ₃	95	294.9	(c)
(8)	B(n-Pr) ₃	156	411.9	(c)

BR₂Cl

(9)	B(CH ₃) ₂ Cl	4.9	176.05	(a)
(10)	B(C ₂ H ₅)Cl	78.5	254.05	(a)
(11)	B(n-Bu) ₂ Cl	173	356	(c)
(12)	BH ₂ Cl	-61	98.05 est. by plot of BR ₂ Cl	

BRCl₂

(13)	B(CH ₃)Cl ₂	11.1	174.15	(a)
(14)	B(C ₂ H ₅)Cl ₂	48	213.25 est. from B(C ₂ H ₅) ₃ → BCl	

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Boiling Points of Boron Compounds (cont.)

	<u>Compound</u>	<u>B.P. (°C)</u>	<u>P</u>	<u>Reference</u>
(15)	B(n-Bu)Cl ₂	108	291.25	(c)
(16)	BHCl ₂	-18	135.25 est. from BRCl ₂ plot	
(17)	17 BCl ₃	+ 12.5	172.4	(b)

From the line for the series BH_nCl_{3-n} (BH₃ → BCl₃), the boiling point of BHCl₂ is about -9°C. Thus, a mean value of -13°C ± 4°C is indicated.

References

- (a) Boron Hydrides and Related Compounds, Callery Chemical Company, January 8, 1951, Dept. of Navy, BuAir, Contract NOa(s) 10992.
- (b) Handbook of Chemistry and Physics, Chemical Rubber Publishing Company.
- (c) Coates, G. E., Organo-Metallic Compounds

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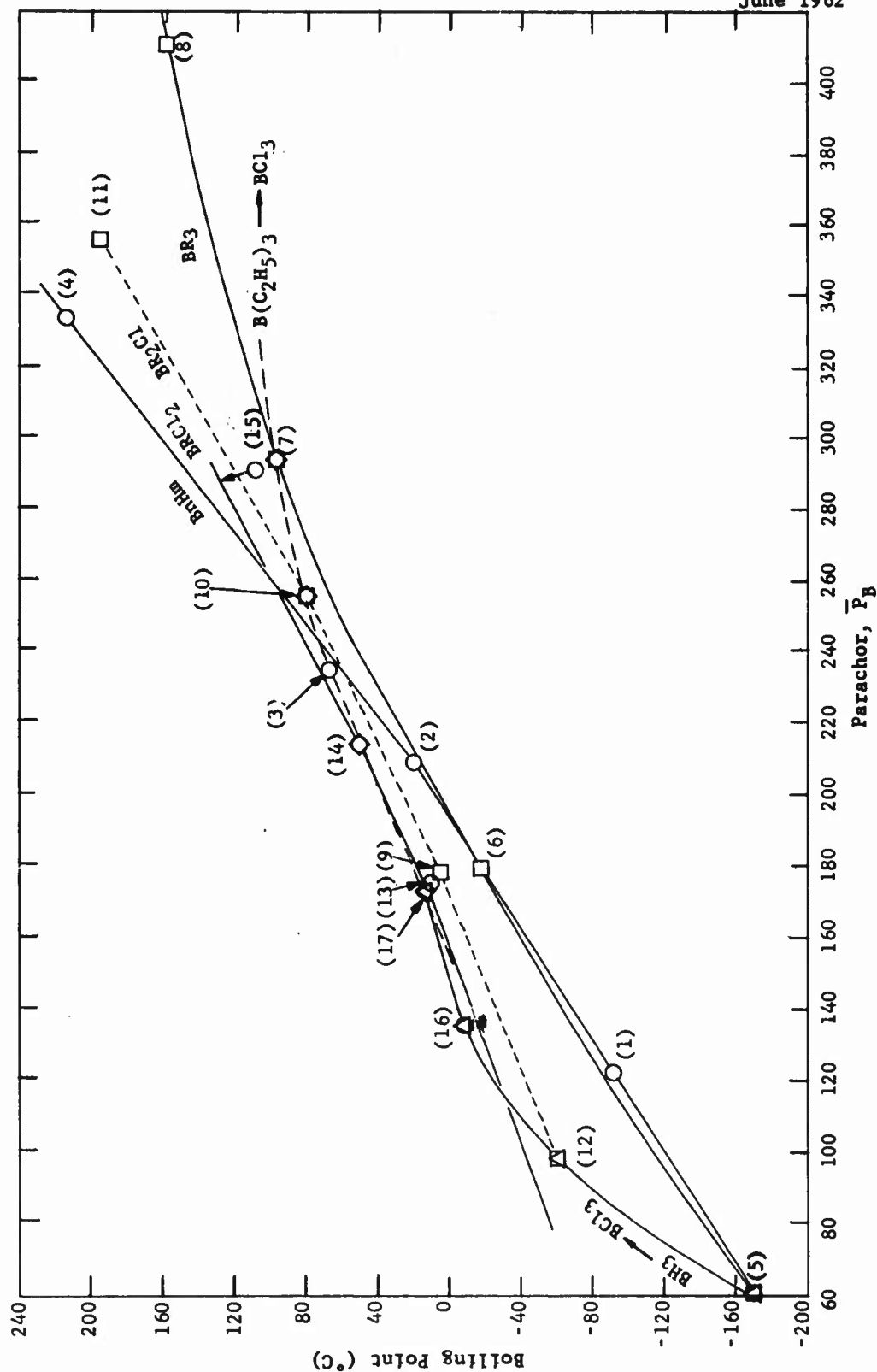


Figure D-1. Boiling Points of Various Boron Compounds

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APPENDIX B

Activity of Hydrochloric Acid in Boron Trichloride

(These graphs compare three sources of data on the
activity of hydrochloric acid in boron trichloride)

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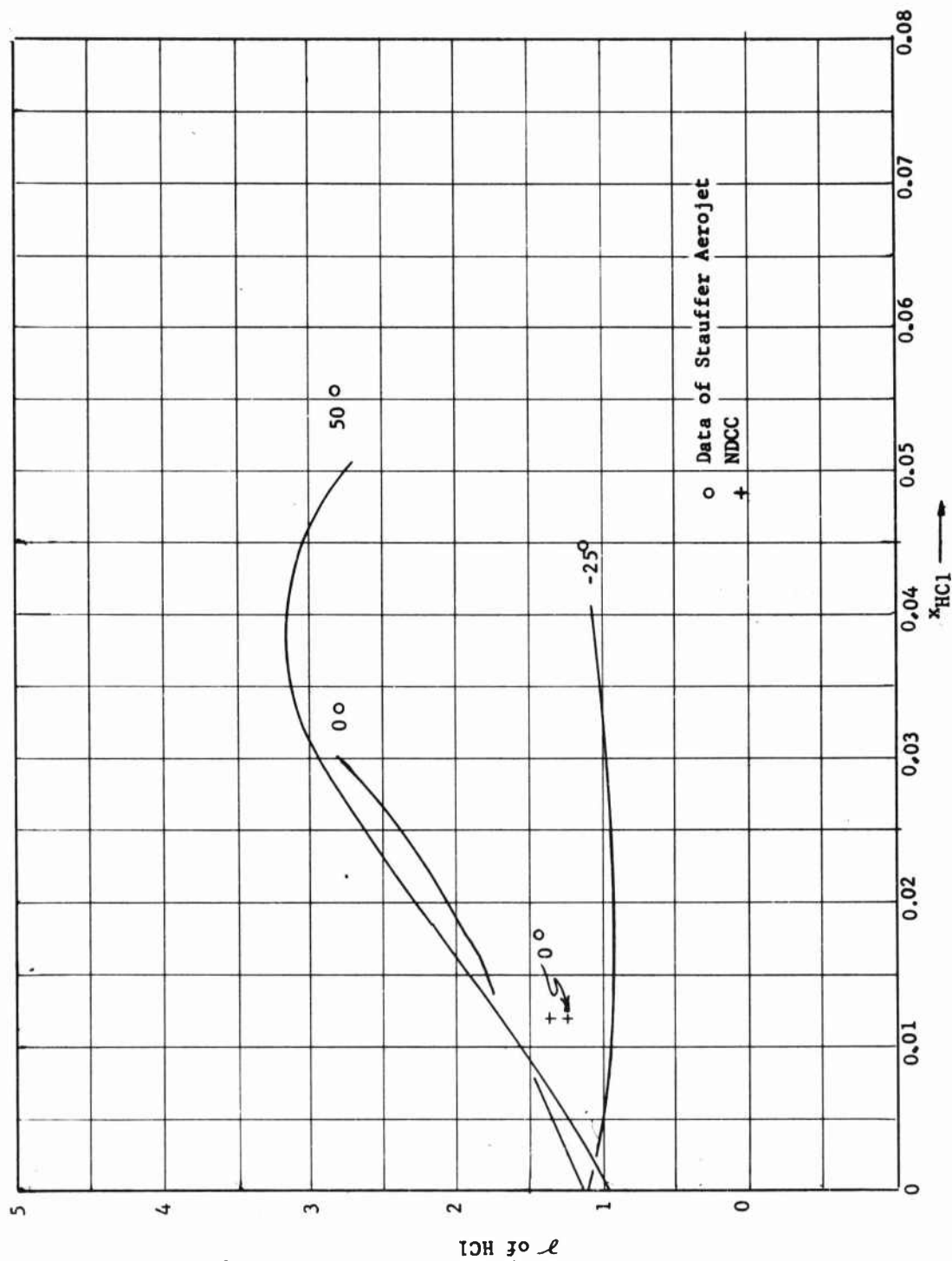


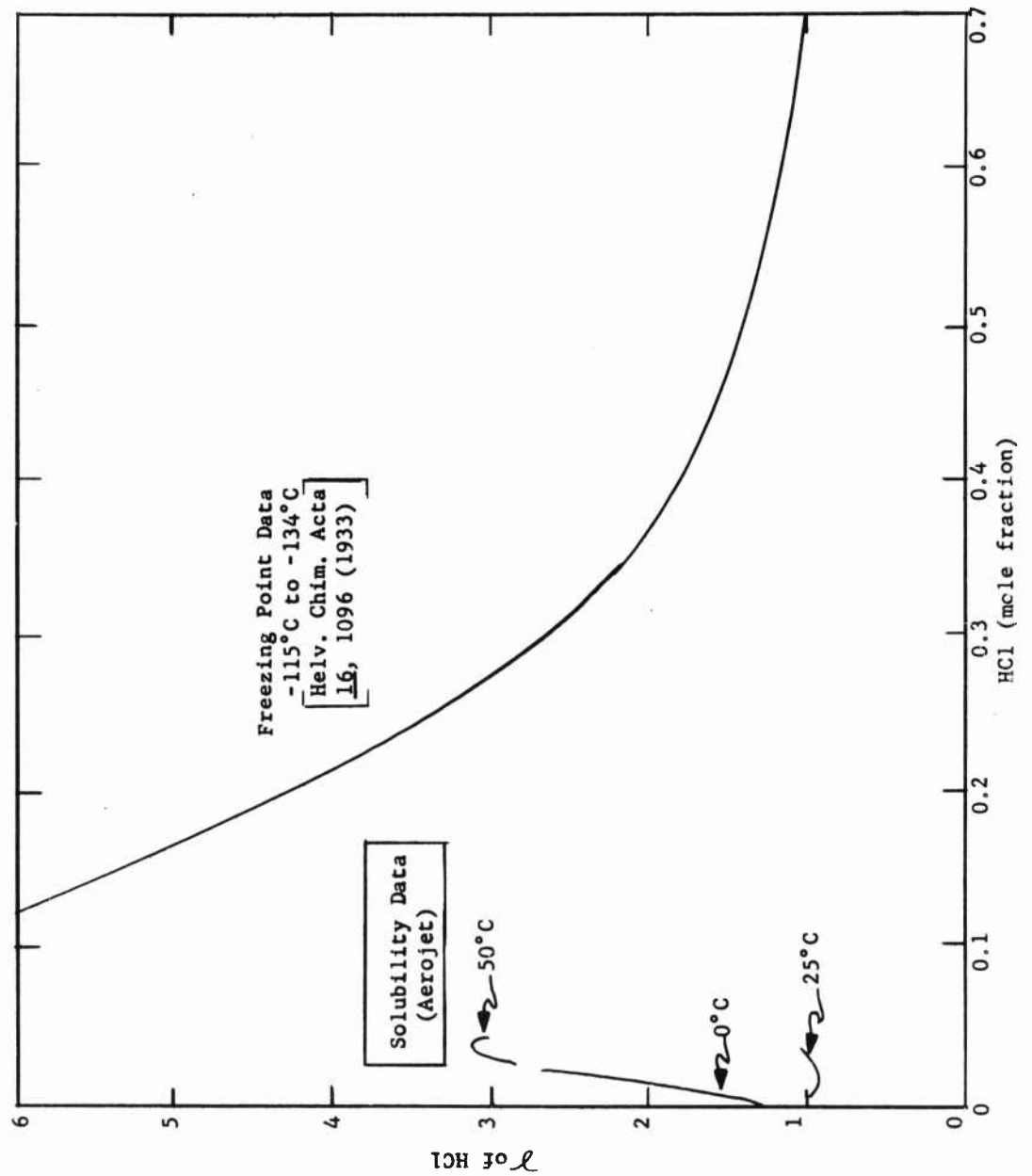
Figure E-1. Activity of HCl in BCl₃ at Various Temperatures
(Low Concentration Range)

E-1

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APPENDIX F

Sampling and Analysis of Process Streams
Prepilot Plant-BCl₃ Hydrogenation Method

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APPENDIX F

Sampling and Analysis of Process Streams Prepilot Plant-BCl₃ Hydrogenation Method

1. Equipment

A. Sampling Arrangements

The arrangements for sampling the prepilot plant streams were an integral part of the piping of the prepilot plant. Thus, as is shown in Figure F-1, samples of flowing streams could be withdrawn at each of five points:

S ₁	Reactor product (or absorber feed)
S ₂	Absorber overhead gas
L ₁	Absorber bottom liquid (i.e., liquid at operating press.)
S ₃	Disproportionator overhead gas
L ₂	Disproportionator bottom liquid (i.e., liquid at operating pressure)

The respective points of withdrawal are indicated by the appropriate letter designation of the valve numbers, S₁R, S₂R, L₁R, S₃R, and L₂R. In addition, samples of the product which were stored in the product collector, Surge Tank Z, could be withdrawn from the process system through the valve, P₅.

Each valve for sample withdrawal actually combined in one body the "straight-through" process stream with controlled take-off through the needle valve seat.

These valves were specially designed to eliminate a space in which trapped process material en route to the sampling line could accumulate between the flowing process stream and the closed seat of the valve. Right angle valves were used.

An extra fitting was welded on to the side of each right angle valve body; and the flowing process stream passed through the valve body at all times, keeping the valve seat flushed.

The sampling manifold was common to all five samples and led to the three sample receivers.

Samples could then be moved from a receiver as desired, passing into the glass apparatus at the point on Figure F-2 which is marked "To Sample Tanks." From this point it could be led to either the left or to the right manifold.

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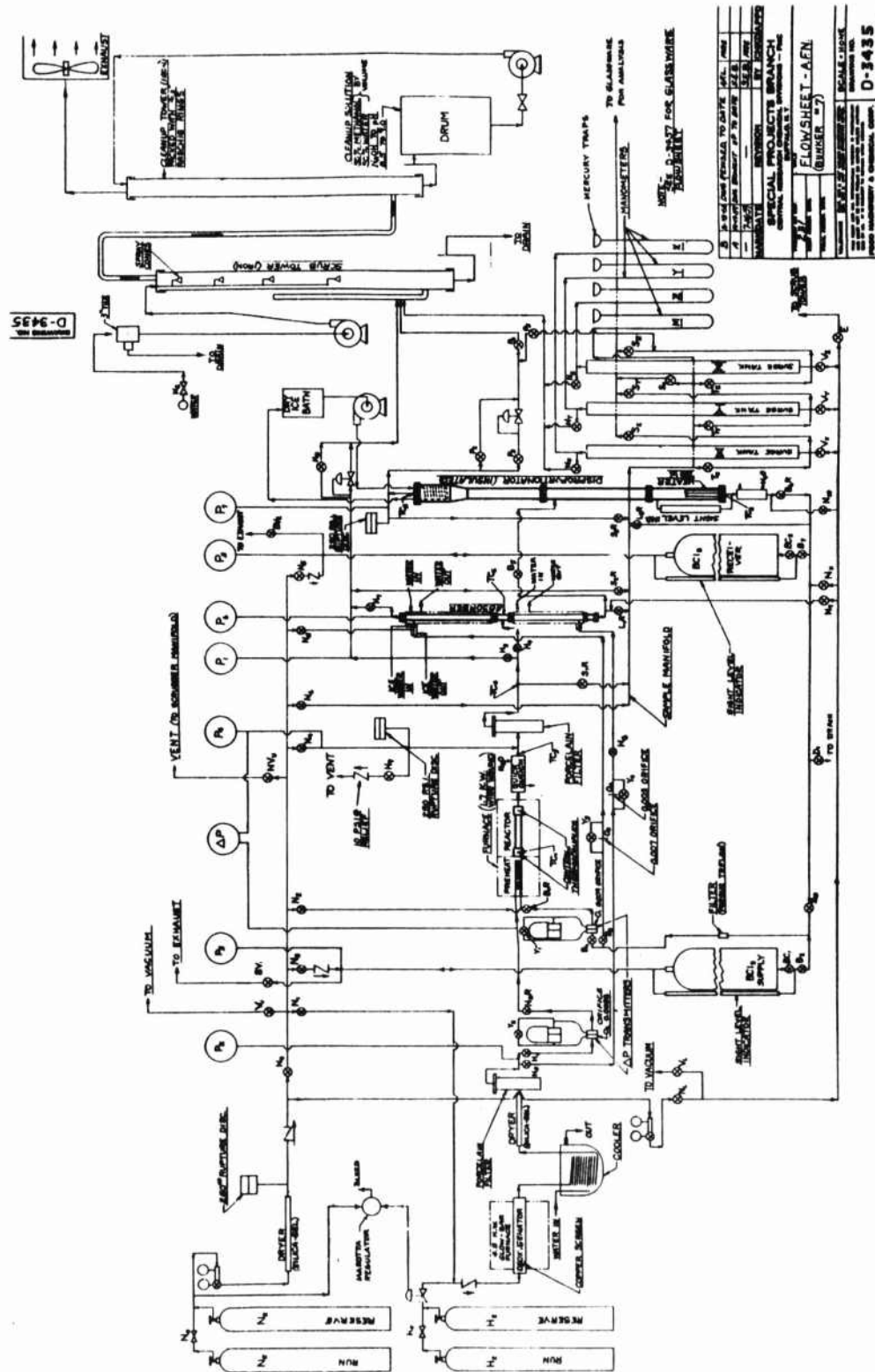


Figure F-1. Schematic Flowsheet: Diborane Prepilot Plant

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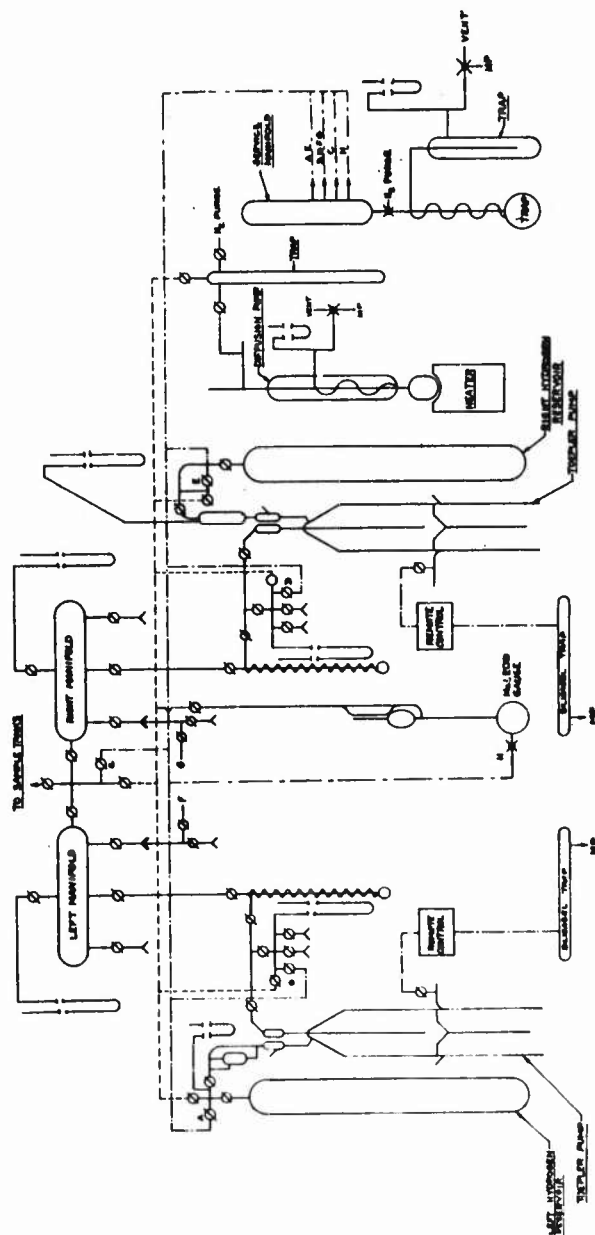


Figure F-2. Schematic Flowsheet: Vacuum-Line Glassware, Diborane Prepilot Plant

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B. Vacuum-Line Equipment

The vacuum-line equipment for measuring and manipulating the sampled materials is shown in the schematic flowsheet (Figure F-2).

The glass vacuum line equipment consisted of several large glass bulbs of measured volumes, various devices for measuring pressure, vacuum and temperature, and three different varieties of pumps: Mechanical (Welch Duo-Seal), (1) Mercury Diffusion, (2) and Transfer (Toepler Pump). (3) There were also a variety of traps of varying efficiencies depending upon their usage. All stopcocks were high vacuum, hollow bore, and all metal-to-glass seals were constructed with Apiezon "W" Wax. Where lubrication was found necessary, Kel-F No. 90 stopcock grease was used. Because BCl_3 reacts readily with rubber, a minimal amount of rubber tubing was used.

Because of the low liquefaction temperature of HCl and B_2H_6 , high efficiency traps were used. In construction, enough space was allowed for placing large dewar flasks around each trap.

The mechanical pump was used to effect a vacuum of 10^{-2} - 10^{-3} mm./Hg. in the entire vacuum line. These mechanical pumps were cleaned frequently and there was a spare pump ready for use at all times during operations in case of a mechanical failure. A separate mechanical pump was used to relieve the main pumps of the job of evacuating large quantities of waste gases and to prevent the formation of mercury chlorides in the mercury diffusion pump. Two large liquid nitrogen traps were placed before each mechanical pump in the vacuum system to prevent contamination of the pump oil.

The mercury diffusion pump should not be started until the mechanical pump has attained at least 10^{-2} mm./Hg. Water or other high boiling liquids occasionally prevented a good vacuum from being achieved; heating the entire area of contamination eliminated this trouble. A vacuum of 10^{-5} mm./Hg. could easily be reached normally.

2. Sampling Procedures

A. Transfer to Surge Tanks

Four of the five samples of flowing process streams were transferred to the surge tanks through the common sample manifold which is shown in Figure F-1. Before each use, this manifold was purged with N_2 , then evacuated to a constant negative gauge pressure which approximated atmospheric pressure as nearly as could be shown by the mercury manometer which was used.

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- (1) Will Corporation.
 - (2) Delmar Scientific Laboratories, DS-7050.
 - (3) Delmar Scientific Laboratories, DS-7030.

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During the time of sampling from the process system the opening of the sampling valve was controlled to allow the pressure within the sampling line and the surge tank to build up at a controlled rate. The rate of sampling was always kept below that rate which would cause a change in the pressure, or a change in the liquid level in that part of the equipment from which the sample was being withdrawn.

The fifth of the five samples of flowing process streams, the diaphragm overhead gas, S_3 , was drawn directly into the glassware and was not stored in a surge tank since the flow at this point was small.

B. Transfer to Glass Vacuum-Line Equipment

Transfer of a gas sample to the glass vacuum-line equipment was always into one of the two manifolds.

The rate of transfer was governed by the regulation of the stainless steel valve at the sample receiver. Progress of the transfer operation was noted by watching the rise in glass manifold pressure as indicated by the mercury level in the manometer to which it was connected.

Before each transfer to the glass vacuum-line equipment, the pressure in the manifold and connecting lines was reduced to 10^{-3} mm. Hg.

C. Measurement of Sample Size

The size of the sample which was collected in the right or left manifold was measured in all instances except when it was intended to withdraw a portion directly into the infrared sampling tube. To permit such measurement, the volumes of the manifolds had been predetermined.

The volumes of the manifolds and reservoirs were calculated from the difference between the weight when evacuated and the weight when filled with water. These known volumes were in turn used to calibrate other manifolds by the transference of dry nitrogen from a calibrated manifold to a manifold of unknown volume at measured temperatures and pressures. In this manner, all volumes used were calibrated with several known volumes as well as against each other. If the volumes to be calibrated included a manometer, a correction was made for the degree of deflection of the mercury level. All temperatures were measured by ordinary thermometers taped on the outside of the manifolds. All pressures were measured by mercury manometers. The approximate accuracy of all volumes obtained by the transfer of nitrogen was $\pm 3\%$.

At the time of actual measurement all stopcocks leading to the manifold were closed and measurements of the pressure and temperature were taken. The number of moles of gaseous sample could then be calculated assuming the ideal gas law.

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D. Disposition of Samples

Four regular analytical procedures were performed to determine the qualitative and quantitative make-up of these gas samples. These were:

- (1) Infrared absorption
- (2) Fraction non-condensable at -196°C
- (3) Gas evolution (H_2) upon hydrolysis of -196°C condensate
- (4) Titrations of dissolved hydrolysis products after hydrolysis of -196°C condensate

3. Infrared Analyses

A. Equipment

Samples of gas for infrared analysis either were drawn directly through the right or left manifold into a gas absorption cell or were drawn into the evacuated absorption cell from the manifold. The absorption cells were 10 cm. long, having sodium chloride windows sealed with glyptal.

The infrared spectrometer had been made by Perkin-Elmer and was their Model No. 112. It was found satisfactory for these routine analyses.

B. Calibrations

Calibrations were made using American Potash & Chemical Corporation BCl_3 , Matheson Company, Inc. HCl , and Callery Chemical Company B_2H_6 . The gases were calibrated singly and in the presence of other gases including H_2 and BHCl_2 to determine any pressure broadening effects.

All accuracy and precision values are liberal estimates and all data are peculiar to the particular infrared spectrometer that was used.

Extinction coefficients for BHCl_2 were obtained from literature and averaged: (1,2)

$$\begin{array}{l} \text{BHCl}_2 \quad (3.9 \mu) - 17.16 \times 10^{-4} \\ \quad \quad (9.1 \mu) - 39.7 \times 10^{-4} \end{array}$$

Any errors introduced by introduction of these coefficients have been considered negligible since no constant differences can be observed when comparisons are made with other data. No pressure broadening effects were observed for BHCl_2 upon the addition of other gases. Because of a random drift in the spectrometer, only approximate wavelengths could be determined. Errors resulting from temperature and pressure measurements were considered essentially negligible.

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- (1) Private Communication, U. S. Industrial Chemicals Co.
 - (2) Olin Mathieson Chem. Corp. Report No. MCC-1023-TR 128, 4 May 1955.

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C. Typical Curves

Typical infrared spectra of samples from the AFN prepilot plant are shown in Figures F-3 and F-4. Analytical bands used are marked with an asterisk and all baselines are constructed.

D. Special Features

Cell deposits of boric acid and glyptal appeared on the sodium chloride windows but they did not interfere with any of the analytical bands. Interferences of carbon dioxide and water were present but minimized by flushing the spectrometer with dry air. No samples showed impurities of silane, phosgene, carbonyls, high boranes, or any of the impurities often found in the raw materials.

A special mixing device was successfully used to determine the infrared absorption of samples which had been condensed before transferring to the infrared absorption cell. This special flask is sketched in Figure F-5.

The complete sample was condensed through Stopcock "A" into the inner tube. The condensed sample was then allowed to warm after the stopcock was closed. The mercury level was then alternately raised and lowered in the 250 ml. outer flask by operation of the leveling bulb. This action agitated and mixed the gaseous mixture.

An alternate mixing apparatus consists of a large manifold into which has been sealed an aluminum foil ball. When the manifold is gyrated, the motion of the loose ball thoroughly mixes the gases.

4. Determination of Non-Condensables at -196°C

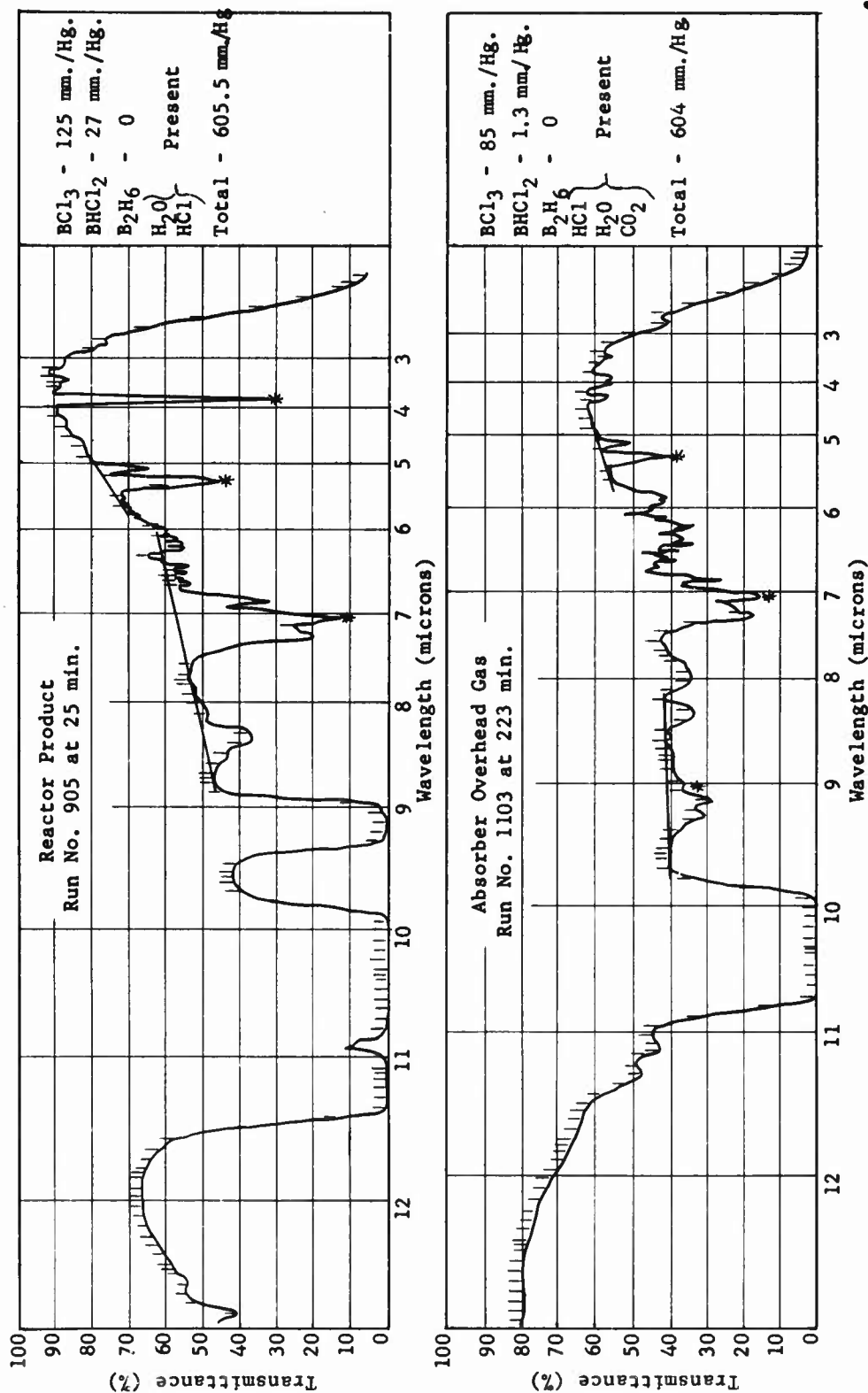
The amount of gas which was non-condensable at -196°C was determined by drawing the contents of the left or right manifold slowly through an efficient trap which was immersed in a Dewar flask filled with liquid N₂. Before the pumping was begun, the amount of gas in the manifold was measured as described earlier.

The non-condensable gas, which was considered to be H₂, was pumped into the appropriate right or left hydrogen reservoir by a Toepler pump. After collection in the calibrated hydrogen reservoir, measurements of pressure and temperature were recorded which enabled calculation of the quantity.

The Toepler transfer pumps were used only to remove hydrogen from a condensed sample and place it in a calibrated volume for measurement. A mechanical pump and relay were used to operate each Toepler pump. Each transfer pump was exactly vertical to facilitate efficient functioning of the valves. After each sample of hydrogen was completely transferred by

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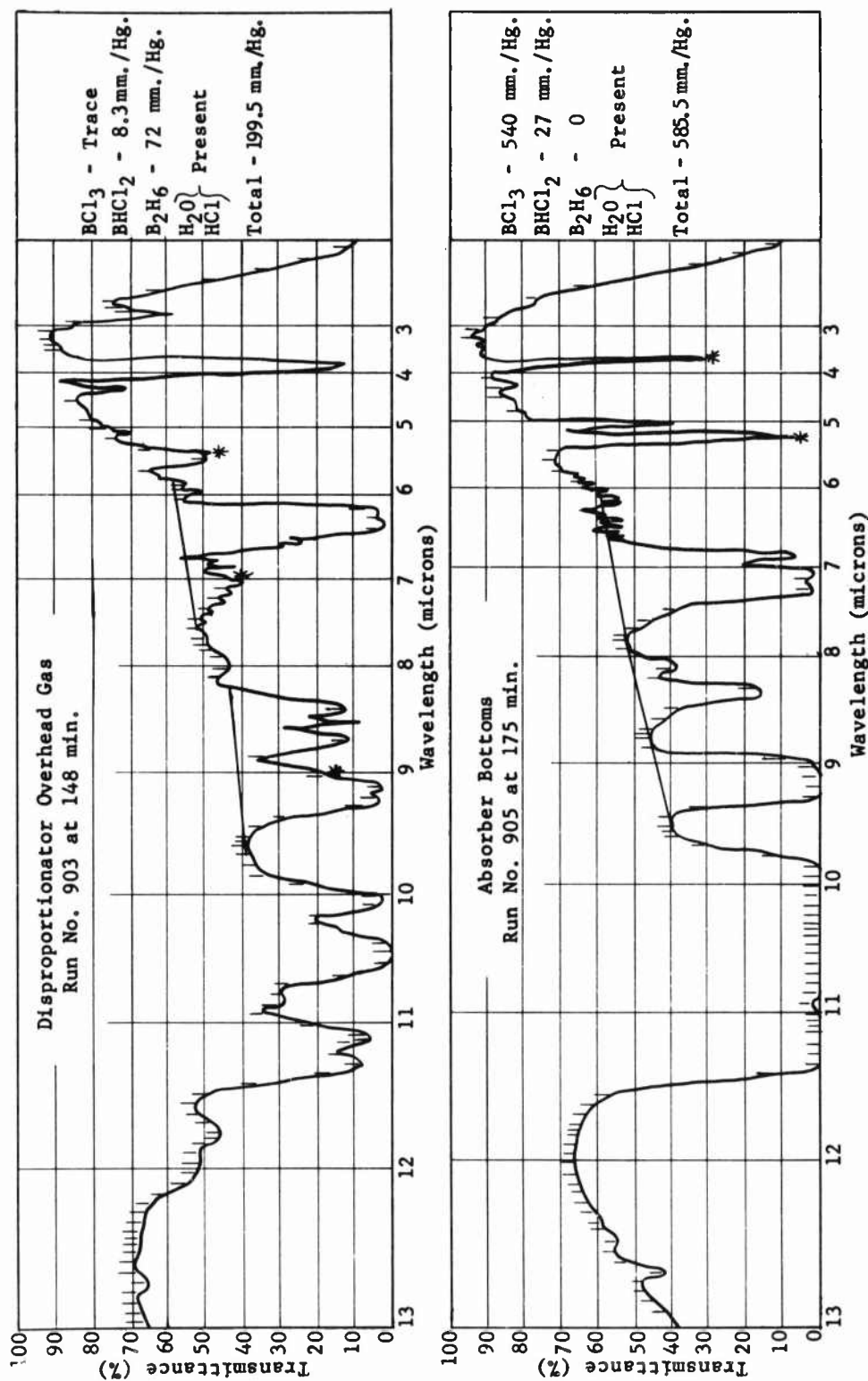
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Figure F-3. Typical Infrared Spectra of Samples from AFN Prepilot Plant

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Figure F-4. Typical Infrared Spectra of Samples from AFN Prepilot Plant

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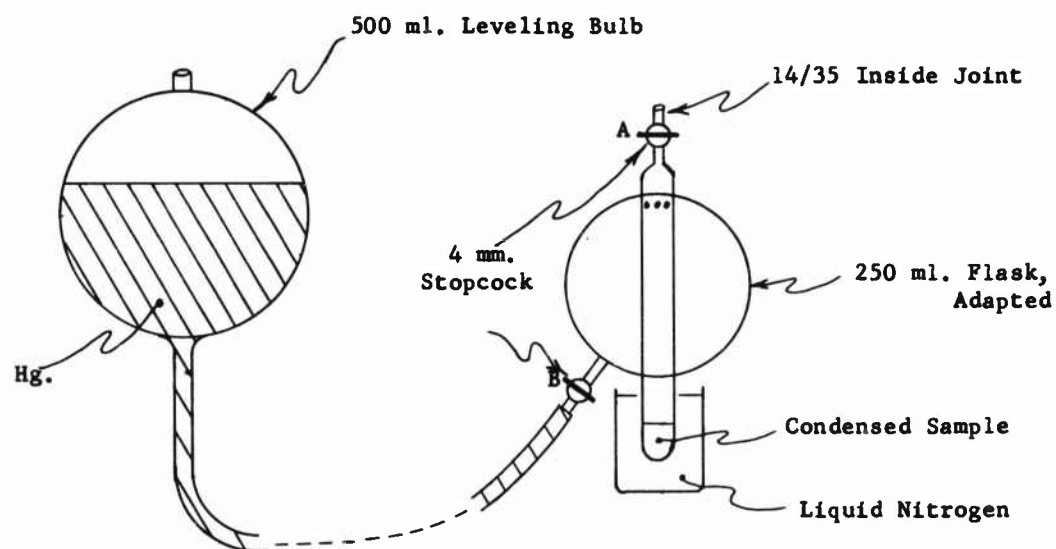


Figure F-5. Special Flask for Mixing Gas Sample Obtained
by Vaporization of Condensed Phase

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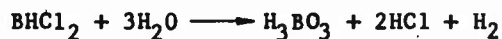
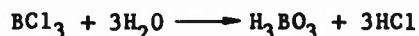
the Toepler pump, the mercury was allowed to rise through the outlet valve to a mark indicating where the level of the mercury was at the time of calibration of the volume. The pressure was then measured and the amount of hydrogen calculated.

The accuracy of this method of analysis is dependent upon the accuracy of the volume calibrations and the measurements of the temperatures and pressures. The accuracy is estimated at approximately $\pm 5\%$. Other coolant temperatures have been unsuccessfully used in attempts to obtain further separation among the components of the original gas mixture.

5. Analytical Chemical Procedures

A. General

By hydrolyzing a measured amount of sample, several analyses can be made on the hydrolysis products. The following reactions occur when a typical sample is hydrolyzed:



All of the hydrolysis products were determined to enable calculation of the composition of the original gaseous mixture.

B. Vaporization and Transfer to Hydrolysis Flask

After the non-condensables were measured, the condensate in the cold trap was allowed to warm and then recondense into an evacuated hydrolysis flask (Figure F-6) containing 50 ml. of ice cooled by immersion in liquid N_2 .

C. Gas Evolution Upon Hydrolysis

The flask was then sealed and warmed and the sample was allowed to hydrolyze with occasional agitation for 4-8 hours to ensure total hydrolysis. The water was then refrozen and the H_2 removed via a Toepler pump to a calibrated reservoir where it was measured and calculated as H_2 from hydrolysis.

The factor in this method of analysis which limits sample size is the volume of the hydrolysis flask. By condensing several successive samples of the same composition in the same hydrolysis flask and measuring the H_2 from the reaction of the total, a great amount of sample can be used, thereby increasing the accuracy and range.

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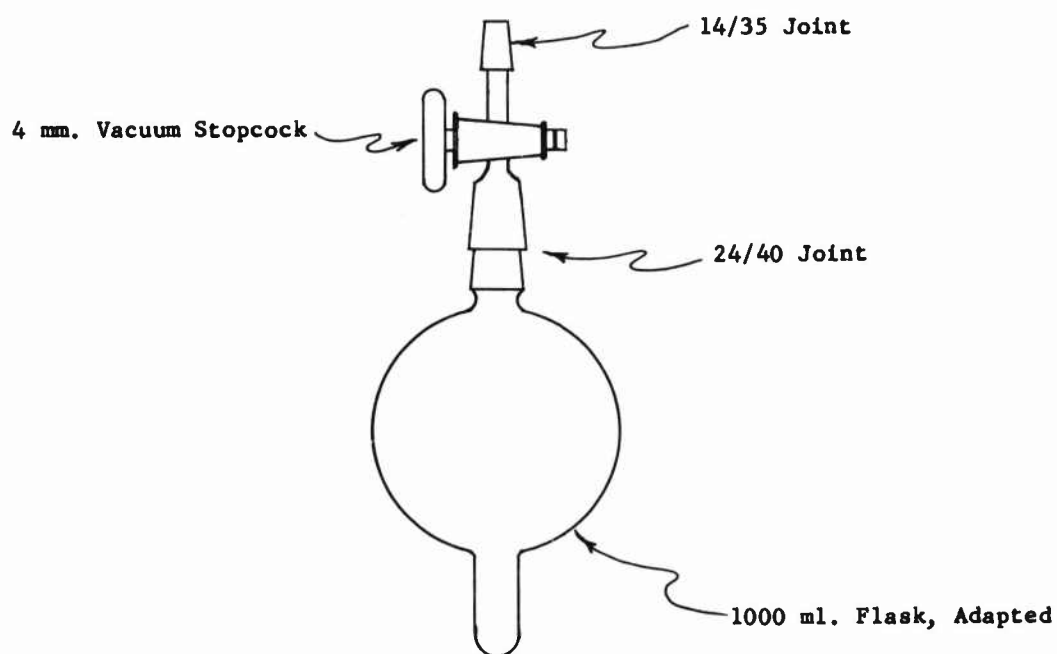


Figure F-6. Special Flask for Hydrolyzing Condensable Components

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There have been indications that the hydrolysis of B_2H_6 is not instantaneous. The approximate accuracy of this analysis is $\pm 10\%$.

D. The Boron Titration

Boric acid, being very weak, cannot be determined by acid-base titration. However, a highly acidic complex is formed by the addition of mannitol. The boron-mannitol complex can be titrated with standard base giving a direct determination of boron.

An appropriate aliquot of the solution of hydrolyzed sample remaining after the H_2 from hydrolysis has been determined was neutralized to a pH of 6. Mannitol was added in abundance and the resulting acidity was titrated with standard 0.1 N NaOH to a pH of 8.

The result of this titration is the sum of H_3BO_3 arising from the hydrolysis of BCl_3 , $BHCl_2$, and B_2H_6 . The amount of BCl_3 can be calculated using values of $BHCl_2$ and B_2H_6 previously determined by infrared analysis and the hydrogen evolved from hydrolysis.

E. The Acid Titration

By titrating with standard 0.1 N NaOH to a pH of 6 an appropriate aliquot of a sample obtained from the hydrolysis of a known amount of gaseous mixture, a measurement of the hydrogen ion concentration was obtained. The resultant value is the sum of the free HCl present in the original mixture and the HCl resulting from the hydrolysis of $BHCl_2$ and BCl_3 . Since the amount of $BHCl_2$ was previously determined either by infrared analysis or by the H_2 from hydrolysis or by both, and the amount of BCl_3 was known from infrared analysis and the boron titration, the amount of free HCl could be calculated.

An alternate method for the analysis of HCl was also used. This was the direct determination of the chloride ion by the classical Volhard Method.* This method was found to be especially satisfactory for liquids having a low chloride ion content. The calculation of results is similar to that of the acid-base titration.

A small amount of free HCl could not be determined in the presence of large amounts of BCl_3 and $BHCl_2$.

* Scott, Wilfred W., Standard Methods of Chemical Analysis, Vol. I, pp. 271, D. Van Nostrand Co., Inc., New York, 1956.

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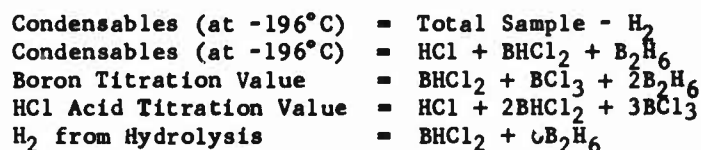
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6. Sample Calculations of Analytical Results

A. General

The following molar relationships exist between analytical results and composition of the original mixture:



These equations can be solved simultaneously or by the substitution of the infrared values for some of the unknown compounds.

However, infrared results usually indicated an absence of one or more of the gaseous components. This enabled the stepwise calculation of each of the components from the above relationships.

B. Reactor Product, S₁, Run 1304 at 35 Min.

(1) Infrared Analysis

The absorption cell for infrared analysis was filled at the same time as the manifold. At the conclusion of filling and at the time the cell was closed off, the pressure was 613.5 mm. By standard methods of measurement and calculation, the infrared absorption curve (similar to Figure F-3) was interpreted to show:

BCl ₃	127 mm. Hg.
BHCl ₂	30.6 mm. Hg.
B ₂ H ₆	0.0 mm. Hg.
CO ₂	Present
HCl	Present

Calculated for incorporation in Table F-1:

$$\begin{aligned}\text{BCl}_3 &= 127 \div 613.5 = 20.7\% \\ \text{BHCl}_2 &= 30.6 \div 613.5 = 4.99\% \\ \text{HCl assumed equal to BHCl}_2\end{aligned}$$

(2) Non-Condensables

Calibrated Manifold Volume : 1098 ml.
Pressure : 613.5 mm. Hg.
Temperature : 23.0°C
Volume Increase Due to
Manometer Liquid Deflection : $\frac{613.5}{40} = 15.34 \text{ ml.}$

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$$\text{Total sample} = \frac{613.5 \times (1098 + 15)}{62.37 \times 296.1} = 36.97 \text{ millimoles}$$

The non-condensable gas was collected in a reservoir whose volume was 2714 ml.

Pressure: 130 mm. Hg.
Temperature: 18.5°C

$$\text{Non-Condensable} = \frac{130 \times 2714}{62.37 \times 291.6} = 19.40 \text{ millimoles}$$

$$\text{Condensable} = 36.97 - 19.40 = 17.57 \text{ millimoles}$$

Calculated for incorporation in Table F-1:

$$\% \text{ Non-Condensables} = \frac{19.40}{36.97} = 52.5\%$$

(3) Gas Evolution Upon Hydrolysis

Volume: 111.7 ml.
Pressure: 277.5 mm. Hg.
Temperature: 18.0°C

$$\text{H}_2 \text{ Gas} = \frac{277.5 \times 111.7}{62.37 \times 291.1} = 1.71 \text{ millimoles}$$

Calculated for incorporation in Table F-1:

$$\% \text{ BHCl}_2 = \frac{1.71}{36.97} = 4.62\%$$

since there was (by infrared) no B_2H_6 in this sample.

(4) Boron Titration

80.50 ml. of 0.1032 N₂ NaOH were required, hence

$$\text{Total B} = 80.50 \times 0.1032 = 8.31 \text{ millimoles}$$

Subtracting B which came from BHCl_2 ,

$$\text{BCl}_3 = 8.31 - 1.71 = 6.60 \text{ millimoles.}$$

Calculated for incorporation in Table F-1:

$$\% \text{ BCl}_3 = \frac{6.60}{36.97} = 17.9\%$$

Note: This differs from the titration value for % BCl_3 as given in Table F-1 which is 17.4%. Unfortunately, all "titration" values for % BCl_3 in Runs 903 through 1401 are in error for the same reason, namely that the wrong value was used for gas law constant in calculating millimoles of gas from P-V-T measurements. This error was discovered too late to justify changing the Tables. Its effects on the argument and the conclusions of this report are slight, however, as is shown in Appendix B, Internal Consistency of Analytical Results.

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(5) HCl Titration

244.1 ml. 0.1032 N NaOH were required, hence,

Total Cl = $242.5 \times 0.1032 = 25.03$ milliequivalents.

Subtracting Cl due to BHCl_2 and Cl due to BCl_3 ,

HCl = $25.03 - 2 \times 1.71 - 3 \times 6.60 = 1.81$ millimoles

Calculated for incorporation in Table F-1:

$$\% \text{ HCl} = \frac{1.81}{36.97} = 4.90\%$$

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TABLE F-1
Complete Tabulation of Analyses, Reactor Products (Absorber Feed)
(Reported as Mole Per Cent)

Run Number Time of Sample (a)	1304				1305		1401	
	35	100	190	345	25	95	20(b)	20
IR Spectrum of Total Gas Sample (ca. 600 mm. Hg. pressure in 10 cm. cell) BCl ₃ BHCl ₂ HCl (assumed) Difference	20.7	19.1	21.0	19.6	18.1	18.3	17.9	17.4
	4.99	5.03	4.98	4.92	4.96	4.87	5.08	5.14
	4.99	5.03	4.98	4.92	4.96	4.87	5.08	5.14
	69.3	70.8	69.0	70.6	72.0	72.0	71.9	72.3
Condensables from Total Gas Sample at -196°C (ca. 36 mg. mole total) Non-Condensables Condensables (by difference)	52.5	68.6	69.2	-	69.0	71.4	-	-
	47.5	31.4	30.8	-	31.0	28.6	-	-
Hydrogen Evolution Upon Hydrolysis of -196°C Condensate BHCl ₂	4.62	5.34	5.70	-	4.20	4.35	-	-
Titration of Hydrolyzed -196°C Condensate (Interpreted on basis of H ₂ evolution) BCl ₃ HCl	17.4	17.2	16.8	-	16.6	17.6	-	-
	4.88	4.29	4.89	-	6.60	3.97	-	-

- (a) Minutes after start of BCl₃ feed to reactor.
(b) Time of sampling marked "b" denotes time from original start of run, prior to backwash of absorbing BCl₃ orifice.

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APPENDIX G

Details of Process Apparatus - Diborane Prepilot Plant

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APPENDIX G

Details of Process Apparatus - Diborane Prepilot Plant

This section is devoted to presenting the details of the process apparatus which made up the integrated prepilot plant.

1. Hydrogen Pre-Treatment

The schematic flowsheet in Figure F-1 of Appendix F shows that the hydrogen from the supply cylinder passes through a deoxygenator, a cooler, a dryer, and a porcelain filter before going to the flow regulating valve or orifice. The pressure in this pre-treatment train was maintained constant at 280 psi absolute.

The deoxygenator consisted of a welded section of stainless steel pipe in which was a rolled-up piece of ordinary copper screening. This tube was heated inside a Glo-Bar electric furnace, whose electricity supply was controlled by on-off regulation to maintain at 1000°F. the junction of a thermocouple which was placed near the wall of the stainless steel tube.

The cooler was a coil of 1/4 inch O.D. stainless steel tubing which was immersed in running cold water.

The dryer was a welded section of stainless steel pipe in which was packed Silica Gel which had been impregnated to indicate wetness by undergoing a color change. The Silica Gel contents of the dryer were often inspected between runs to insure that their drying action was not exhausted.

The porcelain filter was a commercially supplied assembly in which the porous element was of extreme fineness.

2. BCl₃ Supply

The schematic flowsheet in Figure F-1 of Appendix F shows that the BCl₃ supply cylinder was installed so as to be pressurized by nitrogen at nitrogen manifold pressure and so as to have its level constantly visible in the external sight level indicator. The external sight level indicator was a Jergusson gauge of commercial design for pressure service. A threaded hole in the bottom of the BCl₃ cylinder permitted the piping arrangement to be made which is shown in the flowsheet.

All of the BCl₃ flow from the BCl₃ supply cylinder passed through a piece of porous Teflon which was mounted in a filter flange of special design.

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3. Flowmeters

The recording orifice-type flowmeters consisted of specially mounted orifice plates, Foxboro dP cells for sensing the pressure drop and transmitting a control air pressure signal, and Foxboro recorders which received the signal and recorded the pressure drop on circular charts. The clock motor provided one revolution each 30 minutes, so that a sensitive response to changes in flowrate could be made by the operator.

4. Hydrogenation Reactor

The silver screens which were used as catalyst in the hydrogenation reactor had been punched to 1/2 inch diameter from 20 mesh, 0.014 inch diameter wire, which had been procured either from the Newark Wire Cloth Company or the Cleveland Wire Cloth Company. The screens were packed throughout the length of the reactor at a density of about forty screens per inch.

The thermocouples in both the inlet and the outlet heads of the reactor were quick response, shielded thermocouples from Conax Corporation of Buffalo. Each was placed with the hot junction in the middle of the flowing gas stream at its point of maximum velocity. The portions of these couples which were exposed to the flowing gases were silver-plated to avoid contamination of the other parts of the all-silver system.

5. Quick-Quench

The reactor products passed directly into and through a water-cooled "quick quench." This consisted of a length of 1/4 inch O.D. stainless steel tubing into which had been fitted a silver sleeve and outside of which was a close fitting jacket supplied with cooling water. The length of the cooled section was ten inches.

6. Absorber

The assembly drawing of the absorber is shown as Figure G-1.

The absorber was fabricated from one-inch diameter, stainless steel pipe, to which stainless steel flanges were welded and then "trued" by machining to insure perfect vertical alignment when installed.

The 0.16" x 0.16" Cannon protruded packing was supported by perforated plates containing 19 holes each 1/8 inch in diameter. Provision was made for a height of 15 inches of packing below the feed section and for a height of 21 inches of packing above the feed section. The inlet BCl_3 was distributed onto the middle of the upper packed section directly by the bent, welded-in inlet tube in the top head.

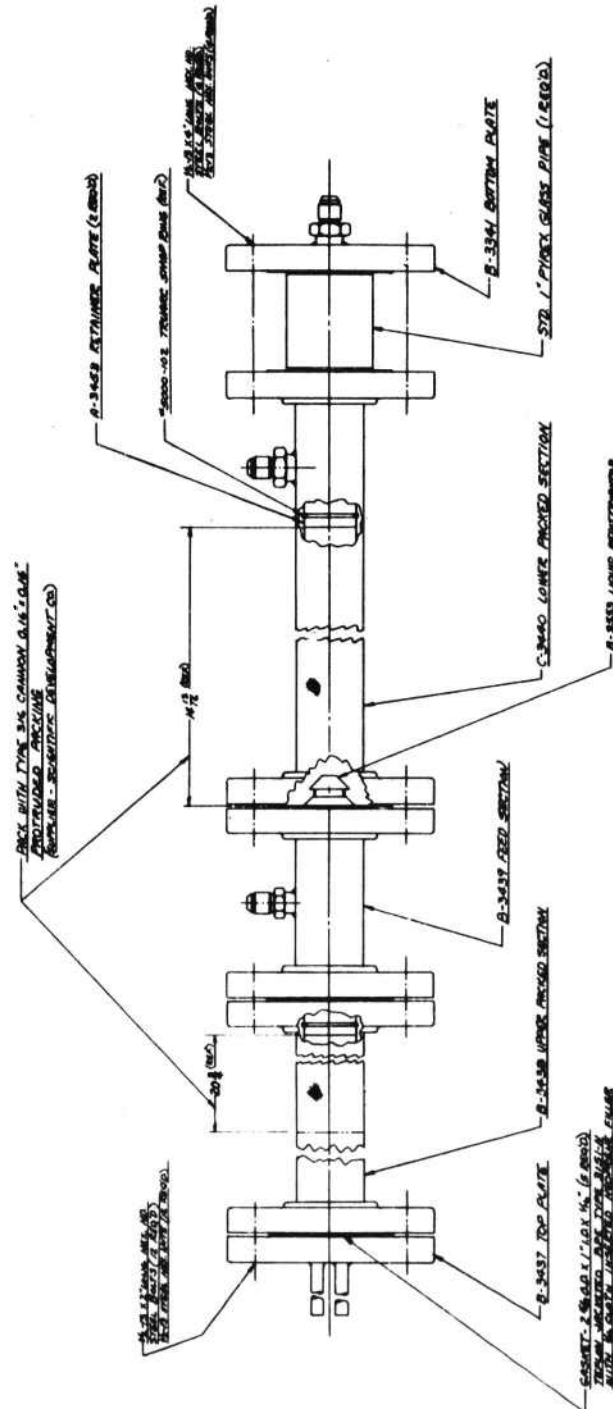


Figure G-1. Absorber Assembly, Diborane Prepilot Plant

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The liquid reaching the lower packed section was at first not specially redistributed. When a redistributor was installed, its location and appearance were as shown in Figure G-1.

The stripping hydrogen inlet was the fitting attachment which is shown just below the lower packing support, and above the Pyrex sight glass on the bottom of the column.

The sight glass on the bottom of the column was a two inch length of standard one-inch Pyrex pipe.

7. Disproportionator

The assembly drawing of the disproportionator is shown as Figure G-2.

The condenser section of this unit was fabricated from four inch stainless steel pipe. The rectification section was fabricated from two inch stainless steel pipe. The two sections were joined, as shown, by a 4" x 2" concentric welding reducer.

The condenser section was packed with three separate concentric double coils of 1/4 inch O.D. stainless steel tubing. The inlet and outlet of each coil passed through the flanged head and were fastened to it by welding. The three coil inlets were manifolded and the three coil outlets were manifolded so that coolant flow through the individual coils was in three parallel paths. Pressure drop through the three parallel coils was maintained at more than 20 pounds per square inch in order to insure that the coolant flowed at satisfactorily high velocities in each coil. The total length of condenser tubing was 52 feet. A disc baffle was placed inside the bottom of the inner coil to prevent the up-flowing gas from having a direct route to the outlet.

The packing in the disproportionator, which was of the same material as the packing in the absorber, was supported on two perforated plates, each having one-eighth inch perforations triangularly spaced on 3/16 inch spacing. The upper packed section was 18 inches high. The lower packed section was 30 inches high. No special arrangements were made for distribution of liquid onto the top of the packing in either section.

The vapor was supplied by boiling the bottoms BCl_3 by use of a Chromalox electric immersion type heater of 750 watts nominal capacity. The electrical input to the heater was supplied by Powerstat variable voltage transformer, but the voltage was not varied during the course of the runs. A measurement of voltage and amperage showed the actual power input had been about 630 watts.

The level of liquid within the disproportionator boiler section was visible in the Jergusson sight gauge, which was connected as is shown in Figure F-1 of Appendix F.

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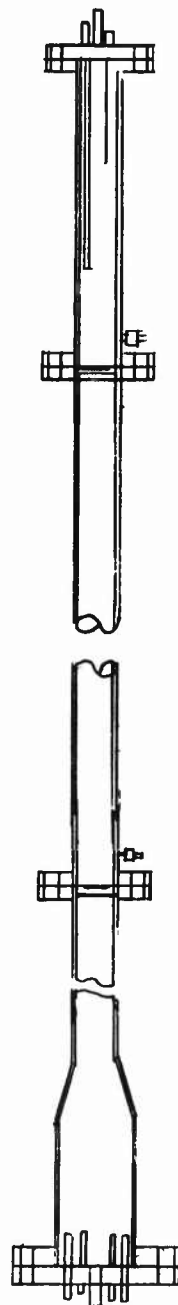


Figure G-2. Disproportionator Assembly, Diborane Prepilot Plant

G-7

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The loss of heat from the disproportionator contents was minimized by use of electric resistance wire in the thermal insulation which covered all but the condenser section. The length of resistance wire was such as was calculated to provide about 80 watts at normal line voltage. This was the magnitude of the heat loss through the insulation which was estimated to occur when the wire, or the metal wall, would be at the temperature of BCl_3 when boiling under 90 psi absolute.

The loss of cold from the condenser was similarly minimized by wrapping coils of tubing to carry flow of the refrigerated coolant under the thermal insulation which was used.

Refrigeration of the circulating coolant was accomplished in three different ways.

First, when the temperature was desired only as cold as ice water, water was circulated through a 100-gallon insulated tank inside of which was a large expansion coil from a refrigerator compressor. The required coolant capacity was greater than that of the refrigeration compressor, so the compressor was allowed to run overnight preceding the run, thereby building up an adequate reservoir of ice in the insulated tank.

Second, when a temperature approaching that of dry ice was desired, solvent grade trichloroethylene was circulated through the annular space between a large container of dry ice and solvent and the insulated wall of a tank. Dry ice was not evaporated directly in the circulating solvent because this led to solution of much CO_2 which, under conditions of reduced pressure in the suction piping to the pump, would come out of solution and cause the solvent to stop circulating. The temperature attainable by this indirect cooling technique proved less than was later desired, hence a third arrangement was then installed.

The third arrangement provided for the circulation of solvent which was chilled by direct contact with dry ice. Sufficient pressure to overcome vapor binding in the sump suction piping was generated by placing the solvent-dry ice tank on the laboratory floor above the prepilot plant and cutting a hole through the floor for the connecting piping. Even with this added pressure, this piping system gave trouble until the pump was mounted on a vertical axis so that there was no horizontal run between the supply tank and the pump suction.

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APPENDIX H

Internal Consistency of Analytical Results

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APPENDIX H

Internal Consistency of Analytical Results

1. Purposes

The purposes of studying the internal consistency of the analytical results in this investigation were to validate analytical determinations of the same quantity made by different methods and to estimate the overall accuracy of conclusions.

2. Bases for Study of Internal Consistency

The principal basis for studying the internal consistency of the analytical results is the material balance assumption that in the process system "input" equals "output".

The other basis is the comparison of infrared results with condensation and "wet method" results determined on the same samples.

To study the consistency of reactor products analyses with reactor feed H_2 and BCl_3 flowrate measurements, it was assumed that all the B which entered the reactor as BCl_3 left the reactor as either BCl_3 or $BHCl_2$; similarly, that all the Cl which entered as BCl_3 left as BCl_3 , $BHCl_2$ or HCl . This assumption can be cross-checked and found to be reasonable by calculating whether the Cl:B ratio in reactor products remained 3:1 as determined by the wet method. This assumption was also cross-checked by the fact that neither corrosion products nor boron degradation products were found in the reactor nor in the connecting piping.

To study the consistency of the reactor product analyses with the disproportionator product analyses, we must also consider:

- A. The question whether all the B-H bonded boron which entered in the disproportionator feed left in the disproportionator product gas.
- B. The possibility that $BHCl_2$ was reconverted to BCl_3 and H_2 by "back reaction" with HCl .
- C. The accuracy of the applicable flowrate measurements.

The fact that in at least 12 runs some of the B-H bonded boron which entered the disproportionator remained therein as liquid B_2H_6 - HCl mixture on the condenser leaves only a few runs which can be used to study the consistency of the reactor product analyses with the disproportionator product analyses.

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The possibility that BHCl_2 was reconverted to BCl_3 and H_2 by back reaction in the disproportionator can be ruled out, because the amount of H_2 in the disproportionator overhead gas was approximately the amount which corresponds to the known solubility of H_2 in BCl_3 as in the absorber bottoms. However, it cannot be similarly ruled out that back reaction occurred in the absorber without citing as evidence a material balance calculation whose validity depends on the consistency of the reactor product analyses with the disproportionator product analyses.

The accuracy of the reactor product flowrate measurements can be partially tested by calculation of feed H_2/BCl_3 ratios from analysis of reactor product gas, as was discussed above. The accuracy of the disproportionator gas product flowrate measurements can be estimated more directly from run measurements than can any of the other flowrates. Another check of this rate is comparison of the calculated flowrate of H_2 in disproportionator product gas with the flowrate of dissolved H_2 in the absorber bottoms, as calculated by multiplying the known solubility of H_2 in BCl_3 times the calculated flowrate of absorber bottoms liquid.

3. Samples from Two-Phase Reactor Product Stream

Abstract of this section: Some of the reactor product gas condensed in the process piping before the point of sampling in 18 of the 25 integrated prepilot plant runs. However, in only ten of these is the probable error serious enough that the reactor product analytical results should not be used in calculations. These are:

Runs 906, 908, 1101, 1102, 1103, 1104, 1203, 1204, 1304 and 1305

Obtaining a representative sample from a two-phase process stream offers difficulties which are well known. Unless very special mechanical arrangements are provided, the differing momentum and wetting characteristics of the two phases cause them to be sampled in a different ratio from that in which they are flowing in the process stream.

For the integrated prepilot plant runs of this investigation, the piping and sampling valves were designed with recognition of the fact that at the desired H_2/BCl_3 ratio of 3.0 the dew point of the reactor product stream would be about 76°F . when the operating pressure was 103 psi absolute. However, it was intended that operating H_2/BCl_3 ratios and stream temperature would be such as to avoid condensation of a second phase.

It was found that in 18 of the 25 runs the temperatures to which the reactor products were cooled, either at quick quench exit or at the sampling point, were below the dew points of the reaction product stream. This occurred in the early runs in which the H_2/BCl_3 ratio unintentionally dropped below 2.8. It occurred in the later runs when, with the combination of lower than 3.7 ratio of H_2/BCl_3 and lower flowrates, the decreasing

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temperature of the cooling water produced lower quick quench exit temperatures. By the time the flowrate was again increased for Runs 1302-1401, the cooling water temperature was even lower, and no steps were taken to raise it.

On the other hand, the reactor product analysis remains useful for selected runs in which enough warm-up apparently occurred due to warm room air to vaporize any condensate. The gravity flow design of the filter and of the intervening piping between the filter and the sampling valve would prevent such condensate from forming pockets and leaving the flowing reactor product stream. As evidence, we show below the H_2/BCl_3 ratios as calculated from infrared determinations for Runs 1301 through 1401. For these runs, the flowmeters were specially reworked and recalibrated, and the metered flowrates were set to provide the same flow ratio in each run.

Run No.	Press. psia	Temperature (°F.)		Calc. "Dew Point Ratio" at Absorber Inlet Gas	H ₂ /BCl ₃ Ratios per Infrared Determinations		
		Quick Quench	Absorber	Temp.	Individual		Ave.
		Exit	Inlet Gas				
1301	103.5	56	70	3.43	3.57, 3.61, 3.29		3.49
1401	103	83	68	3.59	3.35, 3.45		3.40
1302	103.5	65	68	3.59	3.46, 3.41, 3.51		3.46
1303	102	63	68	3.59	3.44, 3.43, 3.44		3.46
					3.53		
1305	108	66	66	3.76	3.33, 3.31		3.32
1304	108	66	65	3.83	2.89, 3.15, 2.84		2.99
					3.08		

On the basis of this list we conclude that the infrared determined ratio is useful for Runs 1301, 1302, 1303 and 1401, but that it is doubtful for Run 1305 and not useful for Run 1304. A tentative generalization would be that for the infrared based ratio to be useful, it should not be exceeded by more than 0.3 by the "dew point ratio" calculated for the temperature and pressure at the point of sampling (the absorber gas inlet temperature).

This tentative generalization would permit the use of the reactor product analysis as representative for the following 15 runs:

903, 904, 905, 907, 1001, 1002, 1003, 1004, 1005, 1201,
1202, 1301, 1302, 1303, and 1401

but not for the following ten runs:

906, 908, 1101, 1102, 1103, 1104, 1203, 1204, 1304 and 1305

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To illustrate the distribution of components which occurs when a liquid phase forms, we present the following calculations based on the data of Run 1304:

- A. Assume true reactor product composition was the same as that of Runs 1302 and 1401, namely: 17.5% BCl_3 , 5.1% BHCl_2 , 77.4% ($\text{H}_2 + \text{HCl}$), or feed $\text{H}_2:\text{BCl}_3$ ratio = 3.42.
- B. At equilibrium at 65°F. and 108 psi absolute, this would form two phases, as follows:

	<u>Vapor</u>	<u>Liquid</u>
Moles per 100 moles reactor Product	96.5%	3.5%
Mole % BCl_3	14.9%	90.3%
Mole % BHCl_2	4.95%	9.67%
Mole % ($\text{H}_2 + \text{HCl}$)	80.15%	0.0%

- C. In order to obtain a sample containing 21.0% BCl_3 ($\text{H}_2:\text{BCl}_3$ feed ratio 2.84, if 5.0% BHCl_2), we would need to obtain a liquid:vapor ratio = 8:92. The resulting % BHCl_2 in the sample would be $0.92 \times 4.95 + 0.08 \times 9.67 = 5.33\%$.
- D. In order to obtain a sample containing 19.1% BCl_3 ($\text{H}_2:\text{BCl}_3$ feed ratio 3.18, of 5.0% BHCl_2), we would need to obtain a liquid:vapor ratio = 6:94. The resulting % BHCl_2 in the sample would be $0.94 \times 4.95 + 0.06 \times 9.67 = 5.23\%$.

This shows that the composition of the reactor product sample for Run 1304 can be explained if it is assumed:

- A. That the feed ratio was the same as for Runs 1302 and 1401.
- B. That at the point of sampling 3.5% of the reactor product was condensed
- C. That 6 to 8% of the actual sample withdrawn was from the liquid phase.

4. Choice of Infrared Analytical Values for Report Calculations

Infrared analyses were chosen in preference to wet method analyses both for total boron and for BHCl_2 throughout the calculations, both because they had been more convenient to obtain and hence were more plentiful, and because they appeared to be more reproducible. In general, the infrared BCl_3 values indicated 5 to 10 per cent more BCl_3 in the absorber

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feed or in the absorber overhead than did the wet method BCl_3 method. In the reactor product analyses for the integrated prepilot plant runs, three of these five to ten per cent can be ascribed to a mathematical error. In the other analysis, containing smaller ratios of $\text{BHCl}_2/\text{BCl}_3$, the effect of the mathematical error is only two per cent.

There is little evidence that the lower value, given by the wet method, might have been more accurate.

5. Reactor Product Analysis vs. Metered Flow Ratio of H_2 to BCl_3

The amount of agreement between the reactor product analysis for total boron and the metered flow ratio of H_2 to BCl_3 is represented fairly by the difference between the metered BCl_3 reactor feed rate and the BCl_3 reactor feed rate which was calculated on the basis of the analytically determined $\text{H}_2:\text{BCl}_3$ ratio.

Only in Runs 1302 and 1303 were the metered H_2 and BCl_3 flowrates well enough calibrated and controlled to be considered for differentiating between the infrared and the wet method analytical results.

- A. H_2 Rate (cylinder H_2 less strip H_2) = 630.5 (average)
vs. H_2 flowmeter = 620
- B. H_2/BCl_3 Ratios (by infrared): 3.46, 3.41 and 3.50 for three determinations in Run 1302; 3.46, 3.44 and 3.52 for four determinations in Run 1313.
- C. BCl_3 Flow = $\frac{630.5}{3.46}$ = 182, or $\frac{620}{3.46}$ = 179
- D. Versus BCl_3 Flow (by flowmeter) = 171
- E. This might be due to high BCl_3 determination (by infrared) amounting to:

$$\frac{182 - 171}{171} \times 100 = 5\% \text{ or to } \frac{179 - 171}{171} \times 100 = 5\%$$

of correct value.

6. Infrared Determination of BHCl_2 vs. Wet Method Determination of BHCl_2

Comparison of BHCl_2 as determined by infrared with BHCl_2 as determined by hydrolysis of the -196°C condensate shows perhaps 10% more BHCl_2 in infrared measurements for hydrolysis values up to 4.6% BHCl_2 . These hydrolysis

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values higher than 5.0% BHCl_2 (Runs 904, 1001 and 1304) are not consistent with infrared results and are presumed to be high due to air leakage-in during the determinations.

7. Reactor Product BHCl_2 vs. Disproportionator Product B_2H_6

The accuracy of the BHCl_2 values as determined by infrared can be estimated in the results of this investigation only by use of the Run 1401A material balance. The good agreement between the value 38.1 for reactor product BHCl_2 and the values $0.7 + 35.6 = 36.3$ for absorber BHCl_2 output or the values $0.7 + 36.7 = 37.4$ for absorber-disproportionator combined output is better than can usually be expected from an estimate of the errors involved in these various measurements and analyses.

8. Ratio Cl:B in Reactor Product by Wet Method

The ratio Cl:B in the reactor product was determined directly by two different but successive titrations on the same aliquot sample. When values for Cl and for B, thus determined, were used for H_2 evolution measurements to calculate BHCl_2 , BCl_3 and HCl , the BHCl_2 value will be found to be equal to the HCl value for those runs in which the 3:1 Cl:B ratio was maintained. Thus: 5.0% BHCl_2 , 5.0% HCl , 15% BCl_3 would have been determined: Per 100 parts sample: 5 parts H_2 evolution, 20 parts B, and 60 parts HCl , wherein Cl:B = 3:1. Note that this $\text{BHCl}_2:\text{H}_2$ ratio in the calculated results should remain 1:1 for Cl:B = 3:1, regardless of whether the measurement of H_2 evolution, for BHCl_2 determination, was correct or whether it was too high or too low.

The mathematical error previously referred to has no effect on validity of this suggested comparison of the HCl and BHCl_2 results. Correcting for that error would create less than a one per cent change in the value presented for mole per cent HCl .

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APPENDIX I

Piping and Instrument Diagrams
Diborane Pilot Plant

C O N F I D E N T I A L

IF-1 & IF-2
REACTOR FEED
HEATER AND
REACTOR

IV-1
FEED
FILTER
1/2" INSULATED 350°F

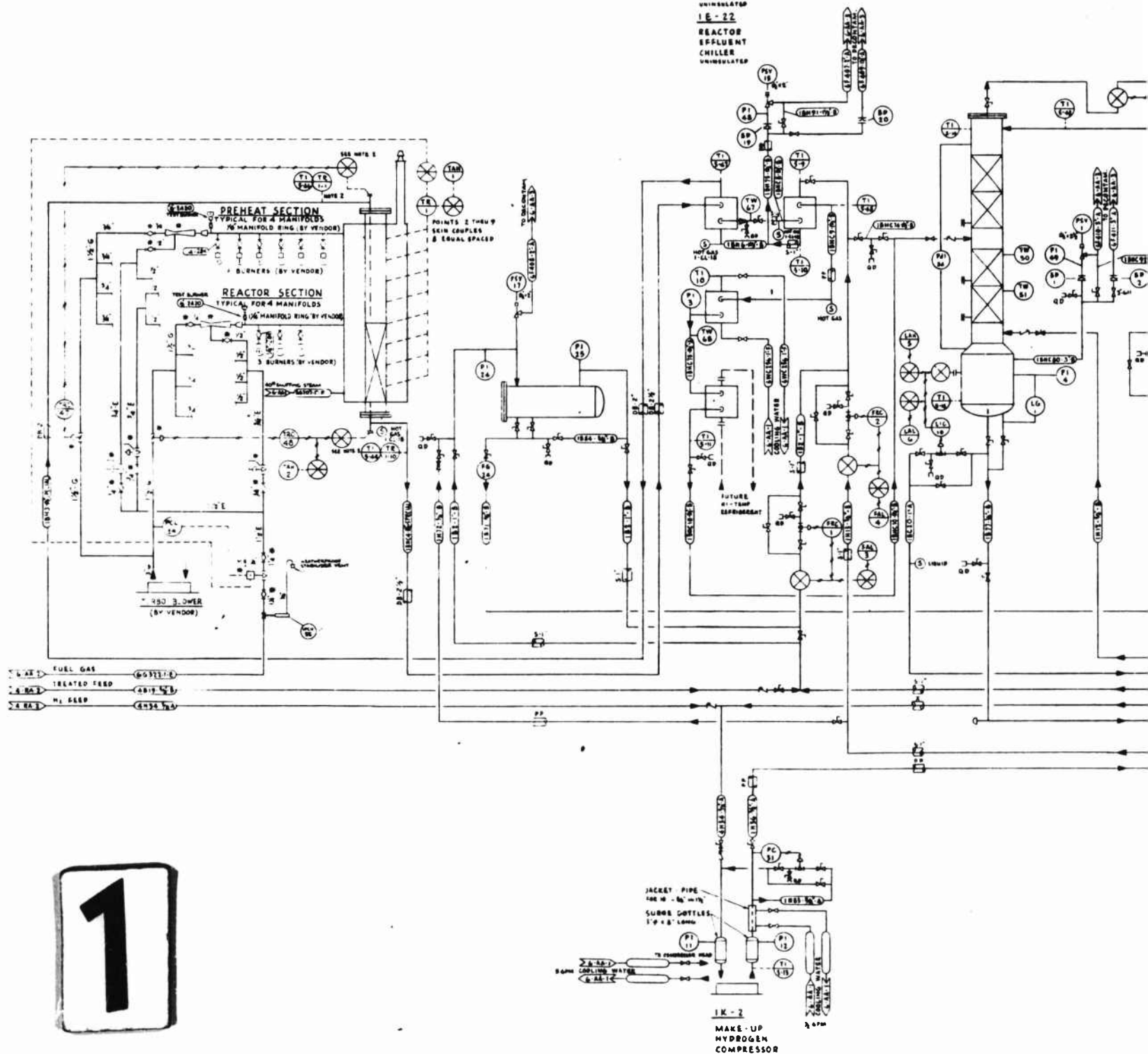
IE-1
REACTOR FEED
EFFLUENT
EXCHANGER
3" INSULATED 350°F

IE-2
FEED
VAPORIZER
1/2" INSULATED 350°F

IC-1
PRIMARY
ABSORBER
UNINSULATED

IE-4
REACTOR
EFFLUENT
COOLER
UNINSULATED

IE-22
REACTOR
EFFLUENT
CHILLER
UNINSULATED



IC-1
PRIMARY
ABSORBER
UNINSULATED

IE-6
RECYCLE
HYDROGEN
COOLER
UNINSULATED

IE-3
PRIMARY ABSORBENT
TRIM COOLER
UNINSULATED

IE-9
SECONDARY ABSORBENT
FEED OR EXCHANGER
UNINSULATED

IC-2
SECONDARY
ABSORBER
27' INSULATED - 50°F

IE-13
SECONDARY ABSORBENT
IM CHILLER
INSULATED - 50°F

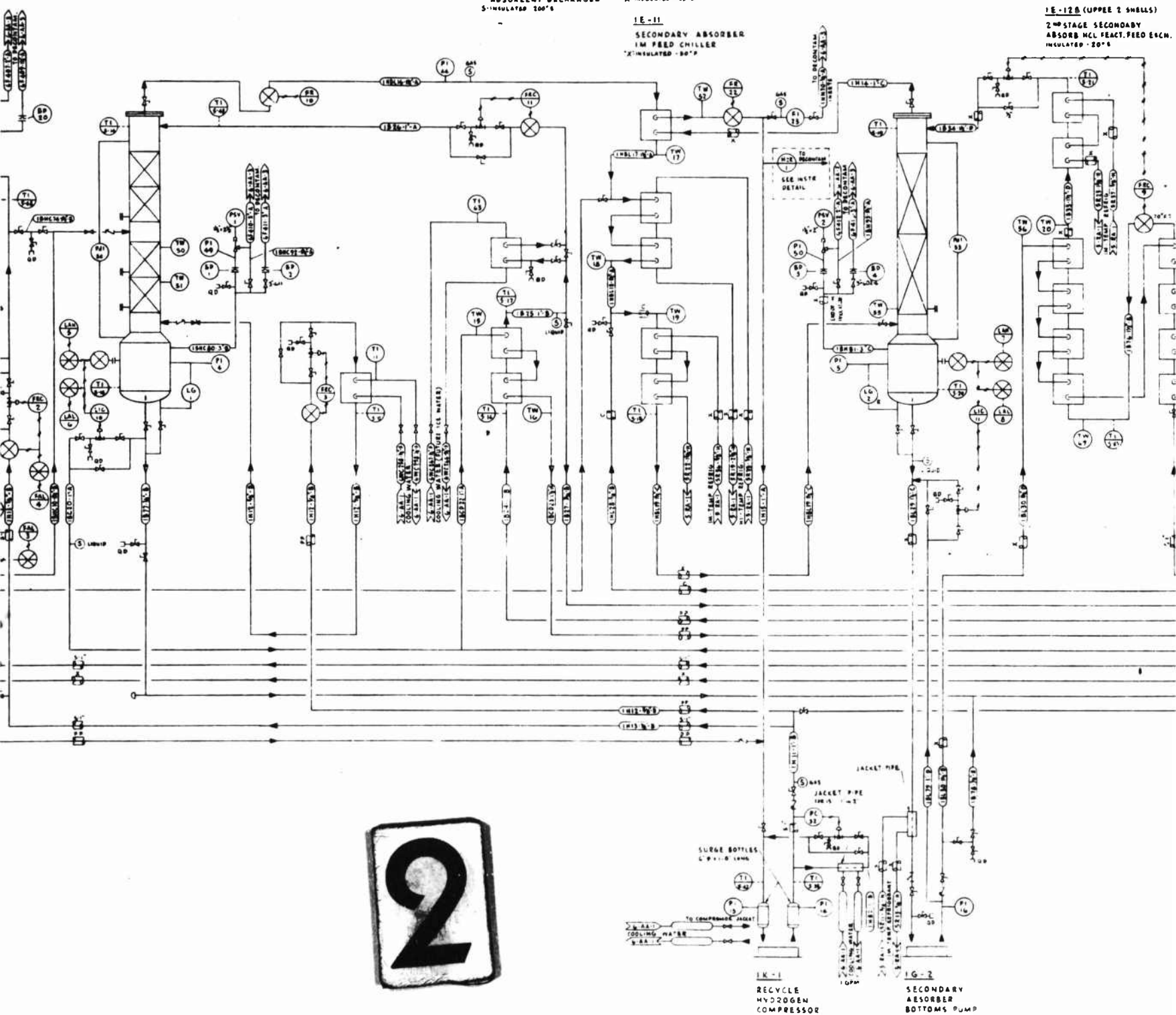
IE-8
PREFRACTIONATOR
FEED PRIMARY
ABSORBENT EXCHANGER
5' INSULATED - 200°F

IE-10
SECONDARY ABSORBENT
FEED CHILLER
X' INSULATED - 50°F

IE-11
SECONDARY ABSORBENT
IM FEED CHILLER
X' INSULATED - 50°F

IE-12A
1ST STAGE SECONDARY
ABSORBENT FEED EXCH.
INSULATED - 50°F

IE-12B (UPPER 2 SHELLS)
2ND STAGE SECONDARY
ABSORBENT FEED EXCH.
INSULATED - 20°F



2

IK-1
RECYCLE
HYDROGEN
COMPRESSOR

IG-2
SECONDARY
ABSORBER
BOTTOMS PUMP

SECONDARY ABSORBER
FEED-ON EXCHANGER
UNIMULATED

SECONDARY ABSORBER
FEED CHILLED
(INSULATED - 32°F)

SECONDARY ABSORBER
IM PBO CHILLER
X-INULATED - 88°F

SECONDARY
ABSORBER
INSULATOR - 50°

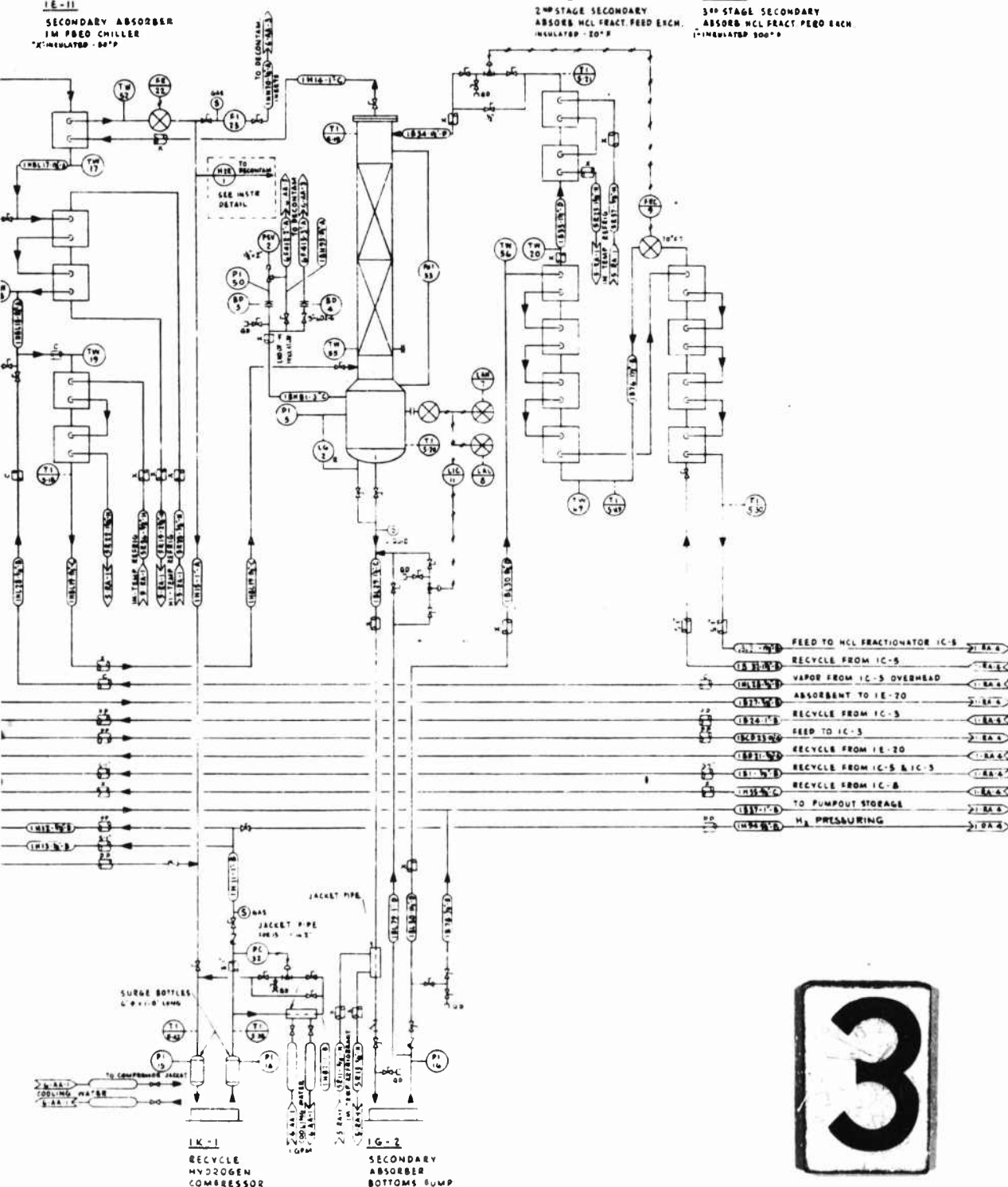
SECONDARY ABSORBENT
IM CHILLER
INSULATED - 90° F

1ST STAGE SECONDARY
ABSOBB. HCL FRAC. FEED EACH.
INSULATED - 50°

2ND STAGE SECONDARY
ABSORB. HCL FRAC. FEED EXCH.
INSULATED - 20° F

2ND STAGE SECONDARY
ABSOBB MCL FRACT FRED EXCH.
UNINSULATED

3RD STAGE SECONDARY
ABSORB NCL FRACT PERQ BRCH
INSULATED 300° F



LEGEND			
PIPING SYMBOLS			
	DATE VALVE		AMEN VALVE
	CLOSE VALVE		SLUD VALVE
	S-WAY VALVE		SPECTACLE VALVE
	CONTROL VALVE (APPLICABLE TO ALL)		CONTROL VALVE (APPLICABLE TO ALL)
	ASSUME EMPTY VALVE		STEAM TRAP
	INSULATION (W/STAINLESS STEEL)		INSULATION (W/STAINLESS STEEL)
INSTRUMENT SYMBOLS			
	LOCAL MOUNTED		TRANSMITTED
	BOOSTER MOUNTED		BOOSTER MOUNTED
	COMBINATION SERVICES		COMBINATION SERVICES
	PROCESS LINE NAME CHANGE		OIL RETURN
	ATTACHMENT CONNECTION		CAPILLARY TUBING
INSTRUMENT IDENTIFICATION			
○ PART NUMBER ○ INSTRUMENT IDENTIFICATION ○ INSTRUMENT NUMBER ALL INSTRUMENTS ARE CODED IN ACCORDANCE WITH THE I & A STANDARD SPECIFICATION NOTES			
LINE IDENTIFICATION			
○ LINE NUMBER ○ P & H ASSOCIATION ○ LINE SIZE ○ SERIAL NUMBER ○ COMMODITY OR SERVICE ○ PLANT NUMBER ○ COMMODITY DESIGNATION			
NOTES			
1 - NICKEL VALVE ON SILVER LINES W/PLATE FOR ENOUGH ARMOR TO BE BELOW 700° OPERATING TEMPERATURE 2 - SILVER COATED MELL 3 - ALL LOW POINTS IN LINES REQUIRING 30 CONNECTIONS SHOULD ALL PROCESS LINES AND AVOID ALL POSSIBLE LOW POINTS AND ELIMINATE ALL DEAD ENDS POSSIBLE 4 - ICL-16 IS A DETAIL OF A HOT GAS SAMPLE DEVICE			

RECHTEL CORPORATION
SAN FRANCISCO

AFN, Inc.
AFN PILOT PLANT, HENDERSON

PROCESS PIPING & INSTRUMENT DIAGRAM
STEP 1 - CATALYTIC HYDROGENATION
REACTION AND ABSORPTION

PREFRACTIONATOR
9-1/2" - PULPITS FOR 100 °F

PREFRACTIONATOR
REBOILER
5-1/2" INSULATE AND 180°

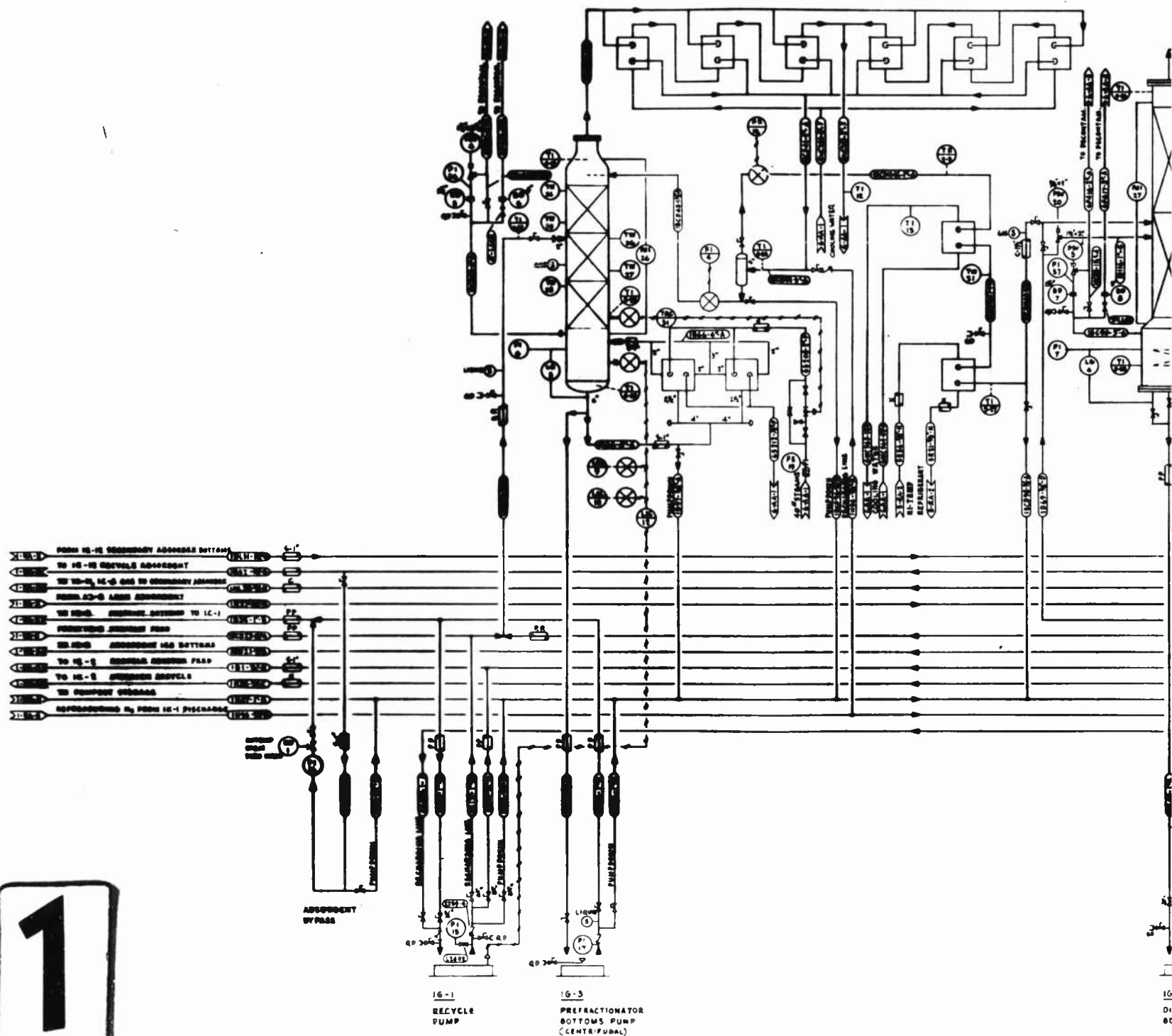
PREFRACTIONATOR
ON CONDENSER
UNINSULATED

**OIS FEED
COOLER
UNINSULATED**

912.
XX-
14.

DIE. FELD
CHILLER
"A"-INSULA

X-INSULATE FOR-207



1E-6

DIS. TOWER
7"X"-INSULATE TOWER FOR -90°F
1 1/2"X"-INSULATE KETTLE FOR R.P.

1E-17

DIS. TOWER
ON CONDENSER
5"X"-INSULATE FOR -90°F

1E-18

NCL FRACTIONATOR
REBOILER
5"X"-INSULATE FOR 300°F

1E-5

NCL FRACTIONATOR
5"X"-INSULATE TOWER TOP 1/2 FOR 15°F
5"X"-INSULATE BALLANCE FOR 300°F

1E-19

NCL FRACTIONATOR
ON CONDENSER
1 1/2"X"-INSULATE FOR -90°F

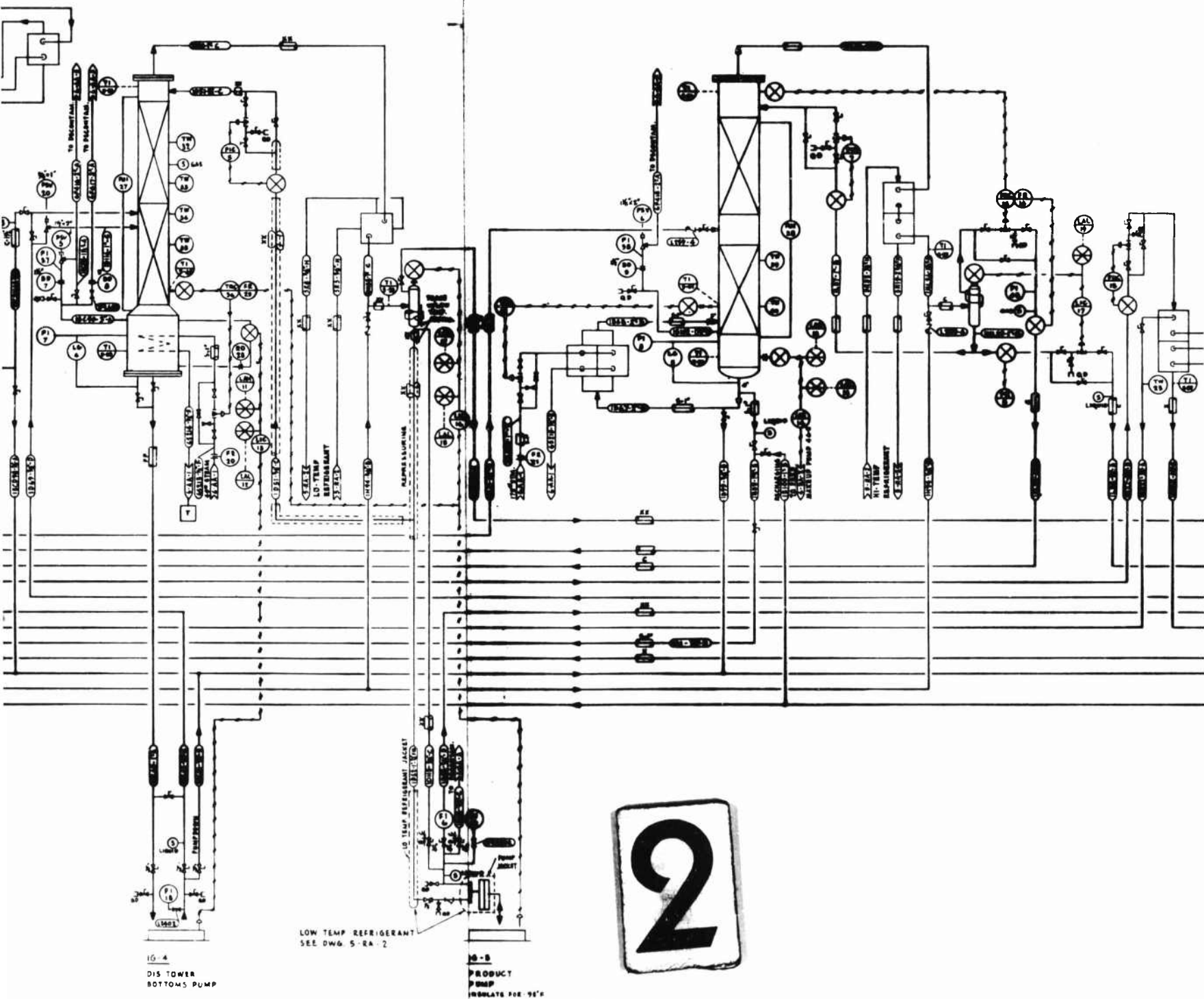
1E-20

FEED BOTTLER
EXCHANGER
(2 1/2"X")-INSULATE

1E-21

FEED BOTTLER
CHILLER
(2 1/2"X")-INSULATE

-207



1E-19
L FRACTIONATOR
H CONDENSER
(2 1/2" X) - INSULATE FOR -20°F

1E-20
FEED BOTTOMS
EXCHANGER
(2 1/2" X) - INSULATE FOR -20°F

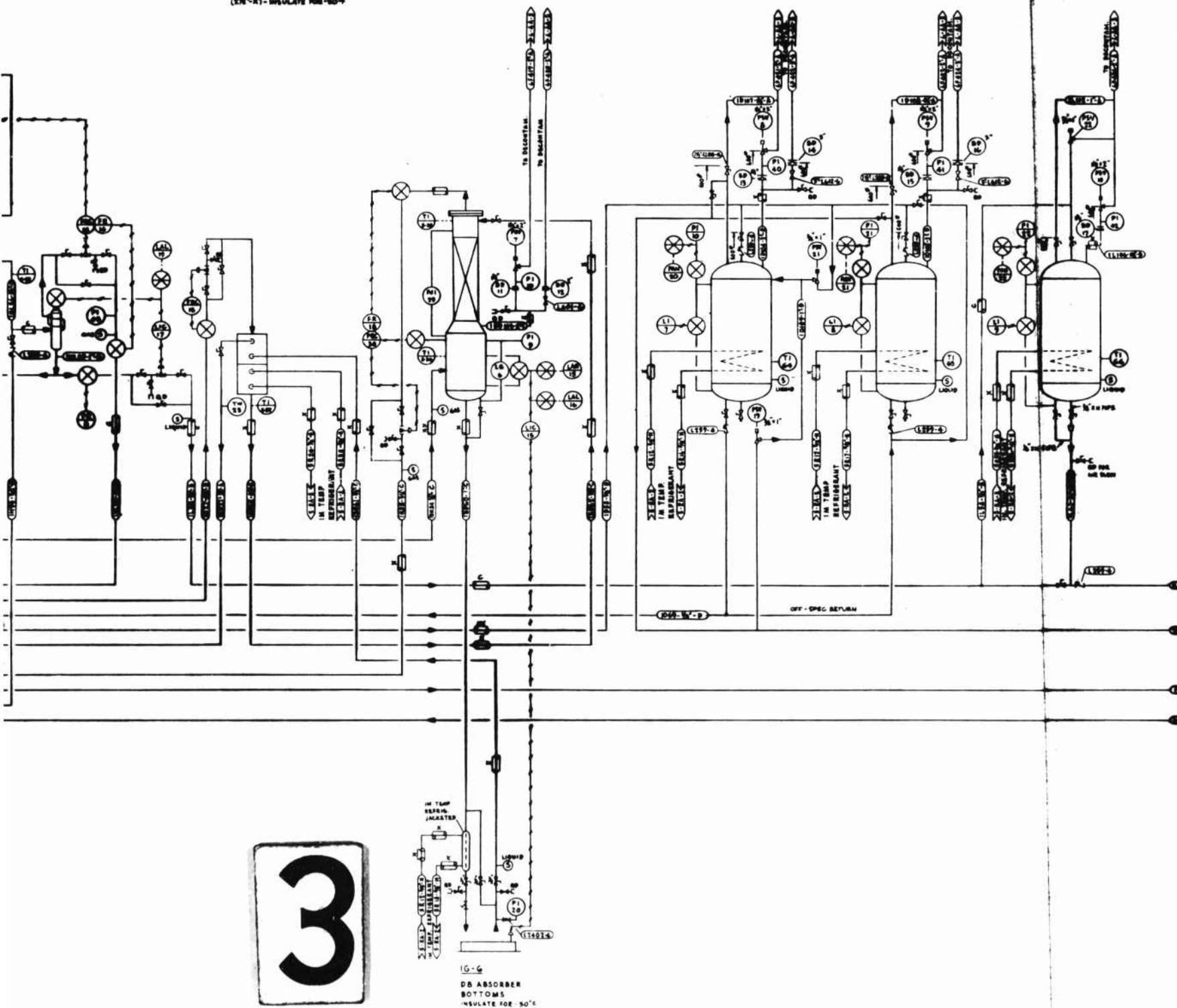
1E-21
D B ABSORBENT
CILLER
(2 1/2" X) - INSULATE FOR -20°F

1C-8
D B ABSORBER
(2 1/2" X) - INSULATE FOR -20°F

1C-7A
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

1C-7B
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

1C-8
D B STORAGE
(2 1/2" X) - INSULATE FOR -20°F

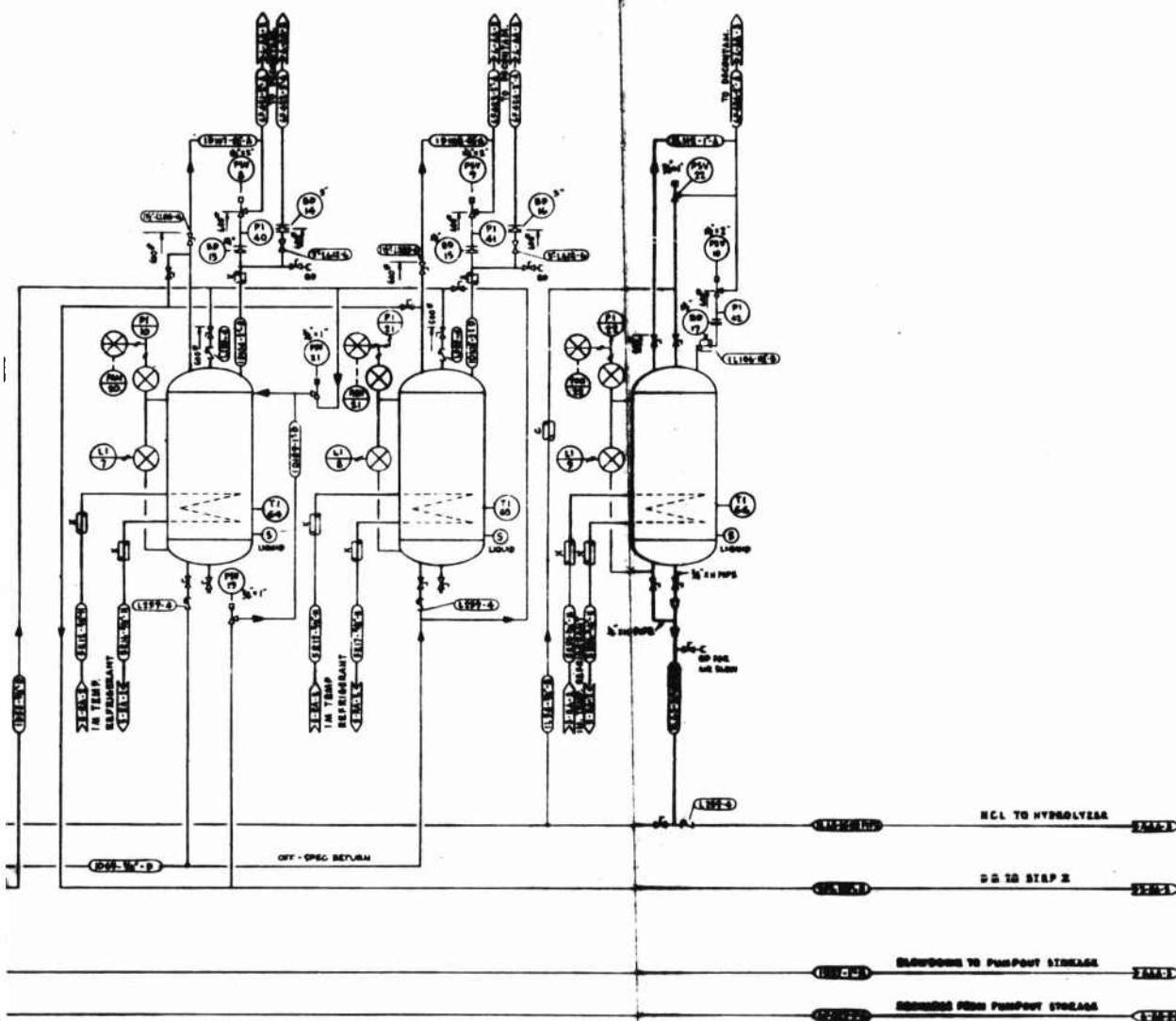


3

IC-7A
DB STORAGE
(2 1/2" X) - INSULATE FOR -20°F

IC-7B
DB STORAGE
(2 1/2" X) - INSULATE FOR -20°F

IC-8
HCL STORAGE
(4 1/2" X) - INSULATE FOR -20°F



PIPING SYMBOLS			
Gate Valve	Check Valve	Plug Valve	spectacle Blind
Block Valve	3-Way Valve	Block Indegment	Sample Connection
Control Valve (Open on Air Failure)	Pressure Safety Valve	3-Way Plug Valve	Insulation (W/Steam Trace)
Insulation (W/Steam Trace)	Insulation (W/Process Protection)	Local Mounted	Transmitter
Board Mounted	Board Mounted Transmitter	Combinational Mount	Electrical Lead
Process Line - Hot Cold	Instrument Control Air	Capillary Tubing	

INSTRUMENT IDENTIFICATION	
Plant Number	Instrument Identification
Instrument Number	
ALL INSTRUMENTS ARE COMED IN ACCORDANCE WITH THE I.S.A. STANDARDS EXCEPT AS NOTED.	

LINE IDENTIFICATION	
Line Number	Piping Specification
Line Size	Serial Number
Commodity or Service	Plant Number
Commodity Designation	

NOTES	
1 - ALL LOW POINTS IN PIPING AND EQUIPMENT REQUIRE 8D CONNECTIONS. SLOPE ALL PROCESS LINES AND AVOID ALL LOW POINTS AND ELIMINATE ALL DEAD ENDS POSSIBLE.	

AFN, Inc AFN PILOT PLANT, HENDERSON PROCESS PIPING & INSTRUMENT DIAGRAM STEP I - CATALYTIC HYDROGENATION DIS SECTION DISTILLATION & RECOVERY			
3192	I-RA-43		

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APPENDIX J

Operating Procedures - Diborane Pilot Plant

C O N F I D E N T I A L

C O N F I D E N T I A L

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APPENDIX J

Diborane Pilot Plant - Operating Procedures

STEP I OPERATING PROCEDURES
AFN Pilot Plant

PREPARATION BEFORE START-UP

- I. Conditions which must be specified before each run.
 - A. Reactor (1F-1,2) temperature (TRC-47, 48) and pressure (PC-31). Latter is established at discharge of make-up hydrogen compressor (1K-1).
 - B. Flow rates of BCl_3 (FRC-1) and H_2 (FRC-2) to reactor (1F-1,2) and thus H_2 flow to BCl_3 ratio.
 - C. Flow rates of BCl_3 (FRC-11) absorbent and H_2 (FRC-3) stripping gas to primary absorber (1C-1).
 - D. Flow rate (FRC-9) of BCl_3 absorbent to secondary absorber (1C-2).
 - E. Recycle hydrogen bleed-off rate (F1-23) or minimum H_2 content determined by H_2 R-1, to maintain satisfactory purity of H_2 feed to reactor (1F-1,2).
 - F. Pressure (PRC-30) of diborane fractionation and absorption system.
 - G. Reflux rate (FI-4) to prefractionator (1C-3).
 - H. Reflux rate (FIC-5) to disproportionator (1C-4).
 - I. Flow rate (FRC-15) of absorbent to diborane absorber (1C-8).
 - J. Pressure (PRC-35) of HCl fractionator (1C-5).
 - K. Reflux rate (FIC-7) to HCl fractionator (1C-5).
- II. Condition of Equipment
 - A. After a normal shutdown the equipment will be under a 20 psig H_2 pressure and isolated into the following sections:
 1. Furnace section - includes 1F-1&2, 1E-1, 1E-2, 1E-4, 1E-22, 1V-1. (The latter may also be isolated following cleaning.)

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2. Primary and secondary absorber section - includes 1C-1, 1C-2, 1E-6, 1E-3, 1E-8, 1E-9, 1E-10, 1E-11, absorbent side of 1E-12, 1E-13, diborane side of 1E-20, suction side of 1G-2 only, 1G-3, and 1G-6.
3. HCl column - includes 1C-5, 1E-18, 1E-19, HCl overhead accumulator, 1G-2, HCl column feed side of 1E-12.
4. Disproportionation section - includes 1C-3, 1C-4 prefractationator overhead accumulator, disproportionator overhead accumulator, 1E-5, 1E-7, 1E-14, 1E-15, 1E-17, 1G-4, suction side of 1G-3, suction side of 1G-5.
5. Diborane absorber - includes 1C-8, feed side of 1E-20, 1E-21, suction side of 1G-6.
6. Diborane storage section (under its own pressure) - includes 1C-7A, 1C-7B, 1G-5.
7. HCl storage - includes 1C-9 and connecting piping from L1CV-17.
8. Compressor section - includes 1K-1, 1K-2.

START-UP

I. Condition of equipment at beginning of start-up.

- A. All equipment is dry, clean (check BCl_3 filter 1V-1), O_2 -free, and under H_2 pressure at approximately 20 psig.
- B. Adequate quantities are on hand of H_2 , purified BCl_3 (or scheduled to be purified) and adequate storage is available for products HCl and B_2H_6 .
- C. The following equipment items have been turned on and are operating:

Destructive scrubber pump (1G-2).

Cooling tower pump (1G-3).

Refrigeration equipment (5V-1) including refrigerant pump (5G-1) and water to condenser (5E-1). See operating instructions.(page J-38).

Air compressor (6K-1) and prepilot plant air compressor.

Vacuum pump (6K-2).

N_2 supply (check level for adequate supply).

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D. Turn cooling water on to the following:

Recycle H₂ compressor (1K-1) and associated aftercooler.
Make-up H₂ compressor (1K-2) and associated aftercooler.
Trim cooler (1E-3) for absorbent to primary absorber (1C-1).
Reactor effluent cooler (1E-4).
H₂ stripping gas cooler (1E-6) to primary absorber (1C-1).
Disproportionator feed cooler (1E-7).
Prefractionator overhead condenser (1E-14).

E. Turn on refrigeration to the following:

1. High temperature (-20°F.)
Secondary absorber feed chiller (1E-10).
Disproportionator feed chiller (1E-5).
HCl fractionator overhead condenser (1E-19).
2. Intermediate temperature (-50°F.)
Secondary absorber bottoms cooler (1G-2 suction
line and jacket)
Secondary absorber feed chiller (1E-11)
Chiller (1E-13) for absorbent to secondary
absorber (1C-2)
Chiller (1E-21) for absorbent to diborane
absorber (1C-8)
3. Low temperature (-100°F.)
Diborane fractionator overhead condenser (1E-17).
Diborane subcooler (suction line and remote head
for 1G-5)
4. Check auxiliary refrigeration unit to determine that
it is properly servicing the following:
Diborane storage tanks (1C-7A,7B).
HCl storage tank (1C-9).
Diborane absorber bottoms cooler (suction and
remote head for 1G-6).
Instrument air dryer (6V-4).

II. Establish a BCl₃ inventory in the system if not already present.

- A. Pressurize with N₂ to 50 psig the selected supply of OK'd,
purified BCl₃ in storage tanks (4C-4A,B,C). Open by-pass
around BCl₃ charge pump (4G-2).
- B. Fill primary absorber (1C-1).
 1. Isolate exchangers 1E-2 and 1E-22.
 2. Open valves in lines 4B19-5/8B, 1B2-1B, and 1BHC74-1
1/2 B, admitting BCl₃ by way of filter (1V-1) to normal
feed point on absorber.

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3. When the correct level is established, close one valve in by-pass line 1BHC74-1 1/2 B.
- C. Fill secondary absorber (1C-2).
1. Open valves in lines 1B32-1 1/2B, 1B76-1 1/2B, 1B33-1 1/2D and 1B34-1 1/2D, allowing BCl_3 to follow the normal absorbent route to this absorber.
 2. When the correct level is established, close the valve in line 1B32-1 1/2B.
- D. Fill prefractionator (1C-3).
1. Open valves in lines 1B40-7/8B and 1B87-1B (by-pass between lines 1B1-7/8B and 1BCD23-1 1/2A). Open valve in line 1BCD23-1 1/2A at column feed point.
 2. When correct level is established, close valve in line 1BCD23-1 1/2A.
- E. Fill disproportionator (1C-4).
1. Open valve between lines 1BC43-5/8B and 1BC49-1A (pump 1G-4 by-pass). Open valve in line 1BC49-1A into column.
 2. When the correct level is established, close pump by-pass valve.
- F. Fill HCl fractionator (1C-5).
1. Open valves in line 1B59-1 1/2B to bottom of column.
 2. When the correct level is established, close these valves.
- G. Fill diborane absorber (1C-8).
1. Open valve in line 1BD21-5/8A and pump 1G-6 by-pass valve (between lines 1BD60-1C and 1BD61-5/8C). BCl_3 comes through line 1BD21-5/8A and 1E-20 by way of line 1BCD23-1 1/2A and exchanger 1E-8.
 2. When the correct level is established, close pump by-pass valve.
- H. Any further BCl_3 additions will be made with BCl_3 charge pump (4G-2).
1. Record liquid level in selected supply tank.
 2. Align valves to pump to Step I.

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III. Establish a BCl_3 flow cycle.

A. Pressurize system.

1. Bring entire system up to 50 psig by opening H_2 trailer supply and by-passing H_2 compressors (1K-1 and 1K-2).
2. Pressurize HCl fractionator (1C-5) to established output of recycle H_2 compressor (1K-1) - 231 psig design.
 - a. Close valves at FRC-2 and FRC-3.
 - b. Open valves in H_2 pressuring line 1H94-5/8B.
 - c. Start compressors. Shut down compressors when output pressure is attained in 1C-5.
 - d. Close valve in hydrogen pressuring line.
(Note: Primary and secondary absorbers are simultaneously brought up to discharge pressure of 1K-2).

B. Utilizing pressure in HCl fractionator (1C-5) establish a BCl_3 flow cycle between this column and secondary absorber (1C-2).

1. Close valve at FRC-1 to prevent BCl_3 from going to furnace section.
2. Set FRC-9 at specified flow rate (design - 4102 lbs./hr.).
3. Start secondary absorber bottoms pump (1G-2).
4. Determine that absorbent to secondary absorber (1C-2) is being properly cooled. Design - -45°F . (TI-5-21)

C. Establish a BCl_3 flow cycle in remainder of fractionation system (excludes reactors 1F-1,2 and associated exchangers).

1. Start prefractionator bottoms pump (1G-3).
2. Set FRC-11 at specified flow rate (design - 2930 lbs./hr.) to establish proper flow of absorbent to primary absorber (1C-1).
3. Set FRC-15 at specified flow rate (design - 352 lbs./hr.) for absorbent to diborane absorber (1C-8).
4. Start diborane bottoms pump (1G-6).
5. Check to see that absorbent to diborane absorber (1C-8) is being properly cooled by chiller 1E-21 (TI-5-37) (Design -45°F .)
6. Check to see that level indicator controllers LIC-10, 12 and 16 are functioning properly.

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- D. Turn on 4G-2 for make-up to enter system as required and as controlled by LIC-14 on HCl fractionator (1C-5).

IV. Establish H₂ flow in the system.

- A. Start H₂ compressors (1K-1,2). Check that discharge pressures of both units are as specified (design - 231 and 151 psig, respectively). WARNING - BCl₃ to secondary absorber must be cold to prevent appreciable quantities of BCl₃ being carried through recycle compressor (1K-1).
- B. Establish specified flow of H₂ through 1E-2, 1E-1, 1F-1, 1F-2, 1E-4, and 1E-22 by setting FRC-2 at specified rate (design - 49 lbs./hr.) and opening appropriate valves.
- C. Establish specified H₂ stripping gas flow to primary absorber (1C-1) by properly setting FRC-3 (design - 20 lbs./hr.) and opening appropriate valves.
- D. Check pressures over entire system and see that all PVC's are controlling at specified pressures (design - 151 psig for PVC-31 at compressor 1K-2 discharge; 231 psig for PVC-32 at compressor 1K-1 discharge; 300 psig for PRC-35 at HCl fractionator overhead; and 72 psig for PRC-30 at diborane absorber overhead).
- E. Start automatic analysis of recycle H₂ by H₂R, thereby providing a small bleed on the system.

V. Heat up fractionating column reboilers.

- A. Prefractionator (1C-3).
1. With cooling water full on to overhead condenser (1E-14), adjust steam to reboiler (1E-15) manually to give reflux at specified rate (design - 5927 lbs./hr.).
 2. Put steam flow controller (TRC-31) on automatic control at a temperature 2°F. below the manually attained level (design - 176°F. at 83 psig).
- B. Disproportionator (1C-4).
1. WARNING - avoid appreciable reflux to prevent under thermal stresses in the low temperature condenser (1E-17).
 2. Set TRC-36 controlling steam flow at normal operating temperature (150°F. est.) and FIC-5 at maximum setting (total reflux).

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3. Check that bottoms heat up properly and that reflux is negligible.

C. HCl fractionator (1C-5).

1. WARNING - avoid appreciable reflux.
2. Set TRC-41 controlling steam flow to normal operating temperature (200°F. est.) and FIC-7 at maximum setting (total reflux).
3. Check that bottoms heat up properly and that reflux is negligible.

VI. Start furnace (1F-1,2) operation.

- A. Check that H₂ flow rate (FRC-2) and purity (H₂R) are as specified.
- B. Set furnace temperature controllers TRC-47 and TRC-48 at 500°F. and light furnace. Follow Special Instructions for this unit. (p. J-25).
- C. Start BCl₃ flow through furnace section when reactor reaches 200°F.
 1. Start BCl₃ recycle pump (1G-1), aligning valves to pump through FRC-1 to furnace section.
 2. Over a period of 15 minutes bring flow rate up slowly by gradually changing setting of FRC-1 until specified rate is obtained (design - 955 lbs./hr.).

VII. Bring plant into operating balance.

- A. Check all controls in plant for proper operation and all flows for steadiness.
- B. When all temperatures, pressures, and flows are well lined out, raise furnace temperatures slowly to specified operating level (design - 1300°F.) per special instructions. Use extreme care in bringing up to temperature to avoid damage to silver-lined equipment.
- C. Establish proper operation of fractionators as BCl₃ conversion takes place.
 1. Prefractionator (1C-3). Frequently adjust set point of TRC-31 to maintain reflux (FI-4) at specified rate.
 2. Disproportionator (1C-4).

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- a. After the top temperature (TI-5-26) drops, and noticeable reflux starts, signifying a diborane content increase, adjust TRC-36 set point to maintain reflux flow rate slightly above the specified level (design = 60 lbs./hr.).
 - b. When TI-5-26 indicates that the tops are pure diborane (design = -70°F. at 76 psig), gradually reduce the setting of FIC-5 to the specified reflux flow rate.
 - c. Select either tank IC-7A or IC-7B to receive the product and record the starting liquid level in the vessel.
 - d. Follow special instructions for H₂ transfer pump for diborane product take-off.
 - e. Continue periodic adjustment of TRC-36 to maintain proper top temperature (TI-5-26) and specified reflux rate.
3. HCl fractionator (IC-5). Follow same general procedure as for disproportionator (IC-4).
 - a. As HCl concentration increases, the temperature at the top of the columns (TI-5-31) approaches the design temperature of 17°F. at 300 psig.
 - b. Periodically adjust TRC-41 to maintain proper top temperature and specified reflux rate (design = 318 lbs./hr.).
 - c. Check that LIC-17 properly controls liquid level in overhead accumulator.
- D. Continuously check all controlled variables and adjust controllers as necessary to keep at specified values.

NORMAL SHUTDOWN

- I. Shut down furnace-reactor (1F-1,2). (See also special instructions for this unit.)
 - A. Utilizing temperature controllers (TRC-47, 48) turn down furnace to low fire setting, then turn off gas supply by closing main block valves adjacent to solenoid operated valve.

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- II. When temperature of reactants leaving furnace (TRC-48) drops to 1000°F., stop BCl_3 flow to reactor. (WARNING: Do not stop H_2 flow.)
- A. Utilizing FRC-1, shut off BCl_3 feed to reactor. Acknowledge low flow alarm (FAL-3).
 - B. Shut off BCl_3 recycle pump (1G-1) and charge pump (4G-1).
- III. As the production of diborane and HCl diminishes and eventually ceases, control the operation of the disproportionator (1C-4) and HCl fractionator (1C-5) accordingly.
- A. Increase the reflux ratio on these columns to maintain product purity by increasing the flow settings on FIC-5 and FIC-7, respectively.
 - B. When the top temperature of either column, as indicated by TI-5-26 or TI-5-31, rises 5 to 10°F. above the normal operating temperature level, thus indicating an impure overhead product despite the operation of the column on essentially total reflux, shut off steam to reboiler by means of the proper controller (TRC-36 or 41). Follow this procedure for both columns (1C-4,5).
 - C. Shut off product pump (1G-5) and disproportionator bottoms pump (1G-4).
- IV. Shut off steam to prefractionator (1C-3) by means of the controller (TRC-31).
- V. Shut off H_2 circulation when reactor temperature (TRC-48) drops to 300°F. or below.
- A. With controller (FRC-2) shut off H_2 flow to reactor. Acknowledge low flow alarm (FAL-4).
 - B. Shut down H_2 compressors (1K-1,2).
 - C. Shut off turbo blower supplying combustion air to furnace. Check that solenoid valve trips.
- VI. Shut off BCl_3 flow in the two circulation loops and through the diborane absorber (1C-8).
- A. Shut off absorbent flow to primary absorber (1C-1) by the controller (FRC-11), and shutting off prefractionator bottoms pump (1G-3).
 - B. Shut off diborane absorber bottoms pump (1G-6).

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- C. Shut off absorbent flow to secondary absorber (1C-2) by means of the controller (FRC-9), and shut off secondary absorber bottoms pump (1G-2).
- VII. Shut down refrigeration unit (5V-1) and pump (5G-1) according to special instructions for that unit.
- VIII. Break up Step I into the following section by closing one valve only in process lines connecting sections (see II-2 under "Preparation Before Start-Up" for list of components).

Furnace Section	Diborane Storage Section
Primary and Secondary Absorber Section	HCl Storage
HCl Column	Compressor Section
Disproportionation Section	Pump-Down Storage
Diborane Absorber	

- IX. Check over pressures in system.
 - A. Diborane and HCl storage sections should be under their own pressures according to vapor pressure of contents at the temperature maintained by the refrigeration unit.
 - B. Other sections should be left under 20-25 psig H_2 pressure. Vent the sections as necessary to attain this.
 - C. With vents closed, check each section pressure for 30 minutes to determine that pressure loss is negligible and system is therefore tight. If pressure drop is detected, remedy cause, repressurize with H_2 and repeat check.

EXTENDED SHUTDOWN (to be designated by pilot plant supervisor)

- I. Follow Steps I through VII for NORMAL SHUTDOWN.
- II. Shut off flow of cooling water to exchangers.
- III. Using N_2 supplied through the QD, blow BCl_3 contained in filter (IV-1) into secondary absorber (1C-2). Flow gauge (FG-24) indicates when filter is empty.
- IV. Empty contents of vessels, along with related equipment and lines, into pumpdown storage tank.
 - A. Purge shutdown storage drum (1C-10) with N_2 , to destruction vent heater, or if it has not been used previously, evacuate vessel and backfill with N_2 three times. Vent drum intermittently as required during filling operation.

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B. Empty primary absorber (1C-1).

1. Using N_2 supply to QD connection at (1G-3), blow absorbent supply line into absorber (1C-1) and into diborane absorber (1C-8).
2. Open bottom connection to pumpdown header and permit vessel contents to drain out. Close valve.
3. Blow bottoms line into prefractionator (1C-3). At same time blow discharge line from disproportionator bottoms pump (1G-4) into pumpdown header.

C. Empty secondary absorber (1C-2).

1. Using N_2 supplied to QD connection at discharge of pump (1G-1) blow absorbent into absorber (1C-2) by way of connections at bottom of HCl fractionator (1C-5).
2. Empty liquid from absorber into pumpdown header by opening connection at discharge of bottoms pump (1G-2).
3. Using N_2 supplied to suction side of pump (1G-2), blow bottoms line into HCl fractionator (1C-5). First vent the fractionator as necessary to the destruction vent header via the overhead vapor line and secondary absorber (1C-2).

D. Empty diborane absorber (1C-8) into prefractionator (1C-3).

1. Blow bottoms through pump (1G-6) to prefractionator (1C-3). Close valve.

E. Empty the prefractionator (1C-3).

1. Open bottoms connection to pumpdown header. Close when empty.
2. Open connection from bottom of overhead accumulator to pumpdown header. Close when empty.

F. Empty disproportionator (1C-4).

1. Drain disproportionator feed cooler (1E-7) and feed chiller (1E-5) to pumpdown header. Close valve when empty.
2. Drain bottom into pumpdown header through pump (1G-4).

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G. Empty HCl fractionator (1C-5).

1. Open bottom connection to pumpdown header. Close when empty.

V. Purge reactor section.

- A. Attach N_2 hose to QD adjacent to FCV-1 and thoroughly purge reactor into primary absorber (1C-1).
- B. Close block valves at inlet to feed vaporizer (1E-2) and at outlet to reactor feed effluent exchanger (1E-1).

VI. Rid remainder of process residues.

- A. Filter (1V-1) primary absorber (1C-1), secondary absorber (1C-2) and H_2 compressors (1K-1,2).
 1. Close block valves at feed point to the prefractionator (1C-3) at discharge of prefractionator bottoms pump (1G-3), at discharge of disproportionator bottoms pump (1G-4), at feed point to HCl column (1C-5) at bottoms outlet of this same column, at discharge of diborane absorber bottoms pump (1G-6), and at inlet to H_2 compressor (1K-2).
 2. Connect N_2 hose to QD at inlet of BCl_3 filter (1V-1) and vacuum hose to QD at discharge of secondary absorber bottoms pump (1G-2).
 3. Open bypasses around all control valves in this system, and around the furnace section (located adjacent to 1D-4). In general, have system open as much as possible.
 4. Alternate between pressurizing the system with N_2 and evacuating until it will hold vacuum when blocked off.
 5. Close all bypass valves.
- B. Prefractionator (1C-3), disproportionator (1C-4) and diborane absorber (1C-8).
 1. With LIC-16 on manual, pump product into designated storage tank (1C-7A or B) until no flow shows on FI-6. Thus overhead accumulator is essentially empty. Shut off pump (1G-5) and close adjacent block valve to storage section.
 2. Close block valves in overhead line from diborane absorber (1C-8) adjacent to (FCV-30).

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3. Open bypasses around all control valves and pumps in this system. Have system open as much as possible.
4. Connect N_2 hose to QD at BD-5 on prefractionator (1C-3) and vacuum hose to QD at discharge of product pump (1G-5).
5. Alternate between pressurizing the system with N_2 and evacuating until it will hold vacuum when blocked off.
6. Close all bypass valves.

C. HCl fractionator (1C-5).

1. Operating LIC-17 manually, empty overhead accumulator into HCl storage tank (1C-9). Close block valves adjacent to LCV-17, and adjacent to PCV-35.
2. Open bypass valves around FCV-7.
3. Through hose connection to QD below BD-9, alternately pressurize the column and evacuate until unit will hold vacuum when blocked off.
4. Close FCV-7 bypass valve.

VII. Pressurize entire system with N_2 to 20-25 psig.

VIII. Isolate various sections of Step I according to Paragraph VIII under NORMAL SHUTDOWN.

IX. Remove temporary hose connections.

EQUIPMENT

I. Primary Absorber (1C-1).

A. Description

Column is carbon steel, 10" dia. and 35' high, 31 ft. of which are packed with 1" Intalox saddles. Uninsulated.

B. Function

Absorb $BHCl_2$ from effluent stream from furnace reactor, while absorbing essentially no HCl.

C. Pressure ratings.

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1. Design pressure - 240 at 200°F.
2. Relief devices
 - a. BD-1, 1-1/2" at 215 psig, backed up by PSV-1, 1-1/2" x 2" at 240 psig.
 - b. BD-2, 3" at 400 psig.

D. Feed Streams

1. Effluent from furnace-reactor, by way of exchangers 1E-1, 1E-2, 1E-4 and 1E-22. Contains H_2 , BCl_3 , $BHCl_2$ and HCl .
2. BCl_3 absorbent from bottom of prefractionator (1C-3) by way of 1E-8 and 1E-3.
3. Stripping H_2 from recycle H_2 compressor (1K-1) by way of exchanger 1E-6.

E. Controls

1. Automatic

- a. Absorbent flow is controlled by FRC-11.
- b. Stripping H_2 flow is controlled by FRC-3.
- c. Liquid level in pot is controlled by LIC-10.
- d. Pressure is determined by PC-31, at discharge of H_2 make-up compressor (1K-2), plus pressure drop through secondary absorber (1C-2).
- e. Feed rate to column is same as reactor effluent and is determined by FRC-1 and FRC-2.

2. Manual

- a. Temperatures of absorbent, stripping gas, and feed stream may be controlled within limits of coolest flow rates to the various exchangers.

3. Analytical

- a. Bottoms analysis by infrared technique indicates quantity of $BHCl_2$ picked up. Presence of HCl in the bottoms liquid is indicative of unsatisfactory column performance as this HCl must eventually wind up with the B_2H_6 product. Detection of HCl at this point is most difficult. Therefore, analysis of the B_2H_6 product, or of the non-condensables from the top of the disproportionator (1C-4) and going to the diborane absorber (1C-8), must be relied upon for control.

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- b. Infrared analysis of the overhead gas indicates if any BHC1_2 has not been absorbed and is therefore lost into the HCl by-product stream.

G. Design Operating Conditions

1. Pressure - 160 psig.
2. Temperature - 90°F. (top)
75°F. (bottom)
3. Flow rates - Feed - 1004 lbs./hr.
Stripping H_2 - 20 lbs./hr.
Absorbent BCl_3 - 2930 lbs./hr.

H. Alarms - low and high level alarms on column bottoms.

II. Secondary Absorber (1C-2).

A. Description

Column is Type 304 SS, because of low temperature operation, and is 8" dia. x 23' high, 17 ft. of which are packed with 1/2" Intalox saddles. The column is insulated with 2-1/2" polyurethane.

B. Function

Absorb HCl from overhead gas stream leaving primary absorber (1C-1).

C. Pressure rating

1. Design Pressure - 240 psig at -50°F. and 200°F.
2. Relief Devices
 - a. BD-3, 1-1/2" at 240 psig, backed up by PSV-2, 1-1/2" x 2".
 - b. BD-4, 3" at 400 psig.

D. Feed streams

1. Overhead gas stream from primary absorber (1C-1), by way of exchangers 1E-9, 1E-10 and 1E-11. This stream is also joined by non-condensable gas from top of HCl fractionator (1C-5). On a mole percentage basis, this combined stream is 80% H_2 , but on a weight basis it is 80% BCl_3 . It contains a small percentage of HCl .
2. BCl_3 absorbent from bottom of HCl fractionator (1C-5), by way of exchangers 1E-12 and 13.

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E. Exit Streams

1. Bottoms liquid, BCl_3 with some HCl , going to HCl fractionator (1C-5) by way of pump (1G-2) and exchanger (1E-12).
2. Overhead gas, to almost pure H_2 , going to recycle compressor (1K-1).

F. Controls

1. Automatic

- a. Absorbent flow is controlled by FRC-9.
- b. Liquid level in pot is controlled by LIC-11.
- c. Pressure is determined by PC-31, at discharge of make-up compressor (1K-2).
- d. Temperature results naturally from intermediate temperature refrigerant fed to absorbent chiller (1E-13) and feed chiller (1E-11).
- e. Feed rate to column is essentially the overhead gas from the primary absorber (1C-1), supplemented by a small amount of non-condensable gas from the HCl fractionator (1C-5).

2. Manual - None.

3. Analytical

Quality of H_2 gas for recycle, coming off the top of the column, is determined by automatic H_2 analyzer (HR-1).

G. Design operating conditions

1. Pressure - 150 psig.
2. Temperature - -45°F .
3. Flow rates - Feed - 878 lbs./hr.
Absorbent - 4100 lbs./hr.

H. Alarms - low and high level alarms on column bottoms.

III. Prefractionator (1C-3)

A. Description

Column is carbon steel 18" dia. x 34' high, 27 ft. of which are packed with 1" Intalox saddles, 1-1/2" insulation for 180°F . External reboiler, 1E-15.

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B. Function

Produce an overhead gas enriched in BHCl_2 (or B_2H_6 if any disproportionation has taken place) and a bottoms product of pure BCl_3 .

C. Pressure Ratings

1. Design pressure - 240 psig at 200°F.
2. Relief devices.
 - a. BD-5, 1-1/2" at 225 psig, backed up by PSV-4, 1-1/2" x 2-1/2" at 240 psig.
 - b. BD-6, 4" at 400 psig.

D. Feed Stream

Combined stream consisting of primary absorber bottoms, and disproportionator bottoms.

E. Exit Streams

1. Uncondensed overhead gas, largely BCl_3 and BHCl_2 , to disproportionator (1C-4).
2. Pure BCl_3 bottoms for recycle to primary absorber (1C-1) and for feed to furnace-reactor (1F-1,2).

F. Controls

1. Automatic
 - a. Temperature in lower part of column is controlled by TRC-31. Controller regulates steam flow to reboiler (1E-15) and therefore determines boil-up rate.
 - b. Pressure is determined by PRC-30, on overhead gas discharging from diborane absorber (1C-8), and by pressure drop through disproportionator (1C-4) and diborane absorber (1C-8).
 - c. Feed rate is controlled by the combined effects of level controllers LIC-10, 13, and 15 on the primary absorber (1C-1), disproportionator (1C-4) and diborane absorber (1C-8), respectively.
 - d. Level in bottom of column is controlled by LIC-12.

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- e. Reflux is automatic in that all material condensed by the overhead condenser (1E-14) is returned to the column as reflux. Rate may be varied by changing set point of TRC-31.

2. Manual

Composition of overhead gas to the prefractionator (1C-4) may be controlled within limits by hand control of cooling water rate to overhead condenser (1E-14).

3. Analytical

- a. BCl_3 bottoms product is checked for presence of BHCl_2 by IR analysis.
- b. Composition of overhead gas is ascertained by IR analysis.

G. Design Operating Conditions

- 1. Temperature - 176°F. (bottom)
156°F. (top)
- 2. Pressure - 82 psig.
- 3. Flow rates - Feed 3800 lbs./hr.
Bottoms 3430 lbs./hr.
Reflux 5930 lbs./hr.
Overhead
Product 370 lbs./hr.

H. Alarms - low and high level alarms on column bottoms.

IV. Disproportionator (1C-4)

A. Description

Upper part of column is Type 304 SS, because of low temperature service, while lower part is carbon steel. Column is 6" dia. x 22' high, 15 ft. of which are packed with 1/2" Intalox saddles. The integral reboiler has 1-1/2" insulation for personnel protection, while the column is insulated for -90°F. with 3' of polyurethane.

B. Function

Complete the disproportionation of BHCl_2 and produce an overhead product of pure diborane. The bottoms composition is not critical.

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C. Pressure Rating

1. Design Pressure - 245 psig at 20°F. Tower is also designed for 225 psig at -100°F.
2. Relief devices
 - a. BD-7, 1-1/2" at 210 psig, backed up by PSV-5, 1-1/2" x 2" at 225 psig.
 - b. BD-8, 3" at 370 psig.

D. Feed Streams

1. Uncondensed overhead gas from prefractionator (1C-3).
2. (Intermittent as required.) Off-spec. product from storage tanks (1C-7A or B).

E. Exit Streams

1. Overhead liquid product of pure diborane to storage tanks (1C-7A & B).
2. Overhead non-condensable gas to diborane absorber (1C-8).
3. Bottoms liquid product, largely BCl_3 with some BHCl_2 , to prefractionator.

F. Controls

1. Automatic
 - a. Temperature in lower part of column is controlled by TRC-36. Controller regulates steam flow to integral reboiler and therefore determines boil-up rate.
 - b. Pressure is determined by PRC-30, on overhead gas discharging from diborane absorber (1C-8), and by pressure drop through that absorber.
 - c. Feed to the column is the total gaseous product of the prefractionator (1C-3) and therefore requires no control.
2. Manual - None
3. Analytical

Product purity is determined by analysis of overhead liquid or gas. IR, chromatographic or wet chemical methods may be employed.

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G. Design operating conditions

1. Temperature - 168°F. (bottom)
- 70°F. (top)
2. Pressure - 77 psig.
3. Flow rates - feed - 373 lbs./hr.
bottoms - 354 lbs./hr.
reflux - 60 lbs./hr.
overhead liquid product - 7.5 lbs./hr.
uncondensed overhead gas - 11.4 lbs./hr. (ca. 50% B₂H₆ by vol.)

H. Alarms

1. Low and high level alarms on column bottoms.
2. Low and high level alarms on overhead accumulator.

V. HCl Fractionator (1C-5)

A. Description

Column is carbon steel, 12" dia. x 26' high, 21 ft. of which are packed with 1" Intalox saddles. The column and reboiler (1E-18) have 1-1/2" insulation.

B. Function

Virtually complete separation of HCl and BCl₃, producing a bottoms product of pure BCl₃, and an overhead of substantially pure HCl.

C. Pressure Ratings

1. Design pressure - 440 psig at 650°F.
 2. Relief devices
- BD-9, 1-1/2" at 400 psig, backed up by PSV-6, 1-1/2" x 2"
at 440 psig.

D. Feed Stream

Bottoms liquid from secondary absorber (1C=2).

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E. Exit Streams

1. Substantially pure liquid HCl from top to storage tank (1C-9).
2. Non-condensable overhead gas recycled to secondary absorber (1C-2).
3. Pure BCl_3 bottoms for recycle to secondary absorber (1C-2) and for feed to furnace-reactor (1F-1,2).

F. Controls

1. Automatic

- a. Temperature in lower part of column is controlled by TRC-41. Controller regulates steam flow to external reboiler (1E-18) and therefore determines boil-up rate.
- b. Pressure is determined by PRC-35, controlling discharge of non-condensable overhead gas.
- c. Feed to the column is the bottoms liquid from the secondary absorber (1C-2) and is regulated by the level controller (LIC-11) on that unit.
- d. Reflux rate is controlled by FIC-7.
- e. Level in the column bottom is controlled by LIC-14.
- f. Level in the overhead accumulator, and therefore the product take-off rate, is controlled by LIC-17.

2. Manual - None

3. Analytical

- a. Overhead product (HCl) purity is determined by analysis of overhead liquid or vapor. IR, chromatographic or wet chemical methods may be employed.
- b. The presence of HCl in the bottoms product cannot be readily detected.

G. Design Operating Conditions

1. Temperature - 285°F. (bottom)
17°F. (top)
2. Pressure - 300 psig.
3. Flow rates - feed - 4915 lbs./hr.
bottoms - 4840 lbs./hr.
reflux - 318 lbs./hr.
Overhead liquid product - 59 lbs./hr.
Uncondensed overhead gas - 13 lbs./hr.

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H. Alarms

1. Low and high level alarms on column bottoms.
2. Low level alarm on overhead accumulator.

VI. Diborane Storage Tanks (1C-7A and B)

A. Description

Vessels are approximately 2 ft. in dia. x 5 ft. high and are made of Type 304 SS. They are insulated with 2-1/2" of polyurethane for -20°F. duty. Their capacity is approximately 100 gallons, or 300 lbs. of product. They have internal cooling coils with refrigeration provided by the auxiliary refrigeration unit (5V-2).

B. Function

Store a week's operating supply of diborane for Step II.

C. Pressure Rating

1. Design - 646 psig at -100°F. or + 450°F.
2. Relief devices
 - a. BD's 13 and 15, 1-1/2" at 530 psig, backed up by PSV's 8 and 9, respectively, 1-1/2" x 2" at 645 psig.
 - b. BD's 14 and 16, 3" at 900 psig.

D. Feed Stream

Overhead liquid diborane from disproportionator (1C-4) by way of pump (1G-5).

E. Exit Streams

1. Gaseous B_2H_6 to Step II.
2. (As needed.) Off-spec liquid B_2H_6 out bottom of tank to disproportionator for rerun.

F. Special Features

1. Refrigeration system is arranged to automatically provide heat if required to maintain adequate vapor pressure in the tanks for feeding Step II.
2. Liquid lines to and from the tanks are equipped with relief valves (PSV's 20 and 21), 3/4" x 1" at 300 psig, to relieve

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pressure in event that slug of liquid is isolated between valves. The gas line from the tanks is also equipped with a relief valve (PSV-19) 3/4" x 1" at 300 psig relieving back into the tank (1C-7A). Note that all these relief valves discharge to a higher pressure, normally 205 psig, and therefore do not open until an actual pressure of 505 psig is attained.

3. Each tank is equipped with board-mounted level indicators (LI-7 & 8) and board-mounted pressure indicators (PI-10 & 21).

G. Controls

1. Automatic

- a. Temperature is maintained at proper level by auxiliary refrigeration system. Control is achieved by Sporlan thermostatic valve.
- b. Pressure is maintained above a minimum level - a switch operating off the board-mounted pressure receiver operates a pair of solenoid valves in the refrigeration system, converting it to a thermal-syphon system transmitting heat into the tank contents. This arrangement is needed to offset the self-refrigeration effect resulting when vapor is taken off the tank to feed Step II.
- c. Filling rate is controlled by LIC-16 on the overhead accumulator for the disproportionator (1C-4).
- d. Withdrawal rate of vapor to Step II is controlled by FRC-1.

2. Manual - None

3. Analytical

Product purity may be determined through a combination of IR, chromatographic, and wet chemical methods.

H. Design operating conditions

1. Temperature - -10°F.
2. Pressure - 205 psig
3. Flow rates - Filling - 7.5 lbs./hr.
Withdrawal - 5.2 lbs./hr.

I. Alarms

High pressure alarms (PAH-20 and 21).

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OPERATING INSTRUCTIONS

A. H₂ Transfer Pump

1. Permit level in 1C-4 overhead accumulator to read 50% or more with design reflux rate.
2. Check and record level in diborane storage tank (1C-7A, 7B).
3. Check valves to insure proper setting for normal reflux.

<u>Valve</u>	<u>Normal Reflux</u>	<u>Preparatory</u>	<u>Transferring</u>
DB Tank Top	Closed	Open	Closed
DB Tank Bottom	Closed	Open	Closed
Storage to 1C-7A or 1C-7B	Closed	Closed	Open
DB Tank Bypass	Open	Closed	Open
H ₂ -DB Equalizing	Closed	Closed	Open

4. Open valve at the top of DB tank in 1C-4 reflux return line in order to vent excess H₂.
5. Open valve at the bottom of DB tank to remove all H₂ and permit entry of liquid diborane into DB tank.
6. Close DB tank bypass valve.
7. Admit H₂ into H₂ pressure tanks until gauge reads 300 psig.
8. Allow DB tank to fill with liquid DB. Check closely any changes in reflux rate and temperature in 1C-4 tops. If conditions are normal, open DB tank bypass and close valves at top and bottom of DB tank.
9. Open valve from DB tank to 1C-7A or 1C-7B.
10. Open equalizing valve between H₂ pressure tanks and DB tank. Transfer is now in progress. Close equalizing valve when H₂ pressure equalizes with that of 1C-7A or B. Close valve from DB tank to 1C-7A or 1C-7B.
11. Open valve at the top of DB tank momentarily in order to vent down to about 75 psig.
12. Check all valve settings for normal reflux.

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FURNACE-REACTOR SECTION (1E-1, 1F-1, 1F-2)

I. Start-Up

A. Establish H₂ flow through reactor.

1. Follow normal start-up procedure for Step I.
2. Set specified flow rate on FRC-2 and check that it and H₂ purity (H₂R) are satisfactory.

B. Prepare to light burners.

1. Open all block valves in furnace firing system other than trim valves on individual burners and the solenoid valve in the gas main.
2. Set control points on TRC-47 and 48 at low end of scale (1000°F.). Put controllers on manual and set air output at 4 psig.
3. Start turbo blower for combustion air and purge combustion chamber for at least 5 minutes.
4. Manually open gas solenoid valve.

C. Light burners one at a time.

1. With aspirators previously set for proper fuel/air ratio, open the trim valve for each burner while holding a Prest-O-Lite torch, or other suitable igniter, at tip of burner, starting at top of furnace and working down.
2. Adjust trim valves as necessary to give approximately equal fire at each burner. Temperatures of skin thermocouples as indicated by TR-1 through TR-9 should be used as a guide.
3. Put controllers (TRC-47 and 48) on automatic and gradually raise temperatures to specified operating level, checking for even temperature distribution as shown by TR-1.

II. Shutdown (See also Step I shutdown procedure)

A. Normal

1. Turn down furnace to low fire setting utilizing controllers (TRC-47, 48), then turn off fuel gas by closing main block valves adjacent to solenoid operated valve.

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2. When temperature of reactants leaving furnace (TRC-48) drops to 1000°F. or below, stop BCl_3 flow to reactor utilizing FRC-1. Acknowledge low flow alarm (FAL-3). WARNING: DO NOT STOP H_2 FLOW!
3. When temperature of reactants leaving furnace (TRC-48) drops to 300°F. or lower, shut off H_2 flow utilizing FRC-2. Acknowledge low flow alarm (FAL-4).
4. Shut off turbo blower supplying combustion air to the furnace. Check that solenoid valve trips.
5. Close all valves in furnace firing system including burner trim valves.

B. Emergency

1. Turn off gas supply to furnace by manually operating micro switch in TR-1 which trips solenoid valve in gas supply line.
2. If emergency condition warrants, shut off BCl_3 and H_2 feeds to reactor by manually closing the control valves from FRC-1 and FRC-2. This procedure is not normally desirable because of the likelihood of damaging the reactor due to lack of cooling provided by the feed stream.
3. If Step 2 above is taken, open steam purge line to furnace to rapidly cool the unit and inert the atmosphere.
4. Follow other steps for normal shutdown as time permits.

REVISED DIBORANE REFLUX AND TAKE-OFF SYSTEM

The diborane reflux and take-off system has been revised (see Fig. 61 in text) to provide improved safety and simpler operation.

This system has been redesigned so as to provide at least two valves between the diborane and the areas that might have to be opened to the atmosphere for repairs. For this reason, four extra valves have been installed in the system. These extra valves, Nos. 3, 11, 12 and 19 in Figure 61, are designated as "Safety Valves" and are to be left open until such time as the system is to be opened to the atmosphere. Since these valves are left open at all times during normal operation, the valve seats should remain clear and a positive shut-off should be insured.

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Normal operation of the reflux and take-off system will be as follows:

1. The entire Step I system is filled, pressurized and the BCl_3 flow cycle established as outlined in the existing Step I Operating Procedures.

2. Set valves as follows:

Valve No. 1	Closed	Valve No. 7	Open
3	Open	8	Open
4	Open	9	Closed
5	Closed	10	Open
6	Closed	11	Open

Establish reflux on the disproportionator (1C-4) in the normal manner.

3. Cool down 1C-7A as far as possible with the auxiliary (Brunner) refrigeration unit, turn on the minus 100 refrigeration to the coils on 1C-7B. After 1C-7B is very cold, shut off the refrigerant going to 1C-7A coils from the Brunner and open the line from both tanks to Step II. Make sure that this line is shut off at the Step II feed point.
4. The line below Valve No. 1 out to the diborane storage tanks should be free of all liquid and contain only pure H_2 or diborane vapors. If any impure material gets into this line, it can be blown out into the bottom of 1C-8 by opening Valves 14, 15 and 16 and then pressurizing the system with H_2 from the pressurizing line (1H 94-5/8B) by opening Valve 2.
5. When the temperatures on the top of 1C-4 and analytical controls indicate that the material in the top of 1C-4 is pure diborane (design - minus 70°F. at 76 psig), gradually reduce the setting of FIC-5 to the specified reflux flow rate and align valves on take-off line as follows:

Valve No. 1	Closed	Valve No. 16	Closed
2	Closed	17	Closed
12	Open	18	Closed
13	Closed	19	Open
14	Open Partly	20	Closed
15	Closed	21	Open

6. When a liquid level has been established in 1C-4 accumulator (check operation of LIC-16), open Valve 1 and adjust Valve 14 so as to maintain a low level in the accumulator.
7. Take off diborane into 1C-7B until the lines to the diborane storage tank are cold, then shut Valve 21 and open Valve 20.

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8. Shut off the refrigeration to 1C-7A, if not done previously (Item 3).
9. With the valves in the prescribed manner, liquid diborane at -100°F . should be put into 1C-7A by gravity flow. Initially, much of the liquid diborane will be flashed off and recondensed in 1C-7B until 1C-7A is cooled down to close to -100°F .
10. In the event of inability to flow by gravity, close the valves on the DB tanks leading to Step II first. Then close Valve 20 and open Valve 21 and attempt to go into 1C-7B by gravity.
11. If either or both tanks cannot be filled by gravity flow, pump (1G-5) will have to be used. Close Valve 14 and open Valves 13 and 15 and start the pump.
12. Throughout run, continue to adjust TRC-36 to maintain proper top temperature and reflux rate. Also adjust Valve 14 (or 1G-5 pump stroke) as necessary to keep minimum practice inventory of DB in column 1C-4.

SHUTDOWN PROCEDURE

- A. As production of diborane decreases, following shutdown of the reactor, increase reflux ratio on 1C-4 to maintain product purity by increasing the setting of FIC-5.
- B. When the temperature on the upper middle portion of 1C-4 goes up $5-10^{\circ}\text{F}$., indicating that the amount of diborane in the column is being depleted, shut off Valve 1 and increase the setting of FIC-5 to the maximum. Then shut off the steam to the reboiler (TRC-36).
- C. Shut off the disproportionator bottoms pump (1G-4, and 1G-5 pump if in use).
- D. Shut down the remainder of the system per standard operating procedures.
- E. Shut down the refrigeration unit per instructions.
- F. Turn refrigerant from the Brunner refrigeration unit into both 1C-7A and 1C-7B.
- G. Shut Valves 20 and 21 after the diborane take-off line has warmed up to ambient temperatures thus vaporizing any diborane left in these lines and recondensing it in one of the DB storage tanks.

Note: In the event that the system must be opened up for any reason, the appropriate safety valves should be closed, the lines vented and flushed with N_2 several times, then pressurized with N_2 and the secondary valves next to the equipment closed.

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OPERATING PROCEDURES

Step IV - BCl₃ Purification

PREPARATION BEFORE START-UP

- I. Place and connect BCl₃ cylinder.
 - A. Use fork lift truck to place cylinder (chlorine type) on weigh scale (4V-2).
 - B. Remove valve protective cover and rotate cylinder on rollers as necessary to place both valves in vertical alignment. Lower valve now connects to the bottom of the cylinder by a dip tube, while the upper valve connects to the vapor space.
 - C. Connect cylinder to the Step IV system.
 1. Connect upper flexible hose to upper cylinder valve.
 2. Connect lower flexible discharge hose to lower cylinder valve.
 3. Open valve between upper flexible connection and QD.
 4. Evacuate and backfill with N₂ each flexible connection, utilizing appropriate QD.
 - D. Record weight of full cylinder.
 - E. Set low weight alarm (WAL-1) 150 lbs. greater than tare weight of cylinder, thus providing for a signal when cylinder is nearly empty.
- II. Conditions which must be specified before each run.
 - A. Charge to column.
 - B. Reflux and product take-off rates.
 - C. Maximum permissible phosgene content of BCl₃ product.
 - D. Maximum permissible concentration of high molecular weight impurities in BCl₃ product. With experience, column temperature may serve as a guide to the build-up of these impurities.
 - E. Distillation pressure.

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START-UP

I. Condition of equipment at beginning of start-up.

- A. All equipment is tight, dry, clean, oxygen-free, and under N_2 pressure at approximately 20 psig.
- B. The following equipment items have been turned on and are operative: Destructive scrubber pump (6G-2) and gas purge on vent system; Cooling tower pump (6G-3) and fan (6V-1); Air compressor (6K-1) and prepilot plant air compressor; Vacuum pump (6K-2); N_2 supply (check level for adequate supply).
- C. Turn cooling water on to the BCl_3 distillation overhead condenser (4E-2A).
- D. Open both liquid discharge and vapor return valves to selected BCl_3 storage tank (4C-2A, B, or C).

II. Charge column (2C-4A) with BCl_3 for batch operation.

- A. Pressurize BCl_3 cylinder with N_2 .
- B. With flow through FC-9 and FI-7 closed, open instrument bypass and permit BCl_3 to flow into column (4C-2A) through normal feed point. Follow weight on scale (4V-2). When last 150 lbs. are going to column, watch weight closely and as soon as weight remains constant and liquid flexible connection vibrates, cylinder is empty.

CAUTION: Minimize nitrogen put into system as this must eventually be vented with accompanying BCl_3 loss.

- C. Change BCl_3 cylinder as necessary to provide the desired charge.
 1. Record weight of empty cylinder.
 2. Close discharge block valve (i.e., instrument bypass valve). Blow N_2 back to cylinder, close cylinder valve, then blow sufficient N_2 feed line to column to give a gas cushion in the line and again close feed line valve.
 3. Evacuate flexible connections and backfill with N_2 .
 4. Disconnect flexible connections to cylinder. (WARNING: Wear mask and gloves). Replace valve cover.
 5. Remove cylinder by fork lift after properly labeling.
 6. Reconnect new cylinder as described in PREPARATION BEFORE START-UP and start flow.

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- D. When column is fully charged as indicated on LG-5, close N_2 supply valve and both cylinder valves. Blow BCl_3 in charge line into column (4C-2A) by connecting vacuum- N_2 hose to QD. It may be necessary to vent pressure in column if excessive N_2 has been put into column. Column pressure should not exceed 25 psig before start-up. Close valve in feed line at column inlet. Record final cylinder weight.

III. Provide cylinder for collection of volatile impurities.

- A. If cylinder from which BCl_3 charge has been removed is empty, disconnect it and remove it from the system as outlined in Section II-C.
- B. If cylinder to be removed is partly full, evacuate and back-fill with N_2 the flexible hose connections to the cylinder. Replace valve cover, label and remove cylinder to storage by lift truck.
- C. Again using fork lift truck, set in place on weigh scale (4V-2) the cylinder designated to receive the top cut, align valves vertically, and set valves to connect top and bottom cylinder valves to the 1-1/2" gas-liquid line. Evacuate connection, then pressurize cylinder with N_2 to approximately 5 psig. Open adjacent block valves to 1-1/2" line. Record starting weight of cylinder.

IV. Heat up column and establish reflux conditions.

- A. Align valves in liquid lines from overhead accumulator for total reflux.
- B. Align valves in vapor line from overhead accumulator to connect to BCl_3 cylinder on weigh scale (4V-2).
- C. Cautiously admit steam to reboiler (4E-3A) to heat up charge. Vent pressure as necessary through vent connection to overhead accumulator to maintain pressure (PI-5) at specified level (design - 52 psig).
- D. Continue to increase steam pressure (PI-22) on reboiler until specified reflux rate is achieved (design - 120 gph). Check operation of pressure controller to maintain pressure at specified level.

V. Remove phosgene-rich cut.

- A. Ascertain phosgene content of overhead material achieved under total reflux condition by IR analysis. Experience may permit estimation with sufficient accuracy from analysis of BCl_3 charged.

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- B. Maintain column on total reflux for 8 hours - then open take-off valve through FI-3A for 4 minutes. This material goes to cylinder on weigh scale. Allow column to return to equilibrium on total reflux (4V-2).
 - C. Repeat Step B until overhead is acceptable for storage. Two cuts will generally give a product cut well under the 0.1% COCl₂ specifications.
 - D. When overhead is considered acceptable for storage, and with column on total reflux, close block valve at northeast corner of structure in line to BCl₃ cylinder-receiver.
 - E. After connecting line to cylinder has drained, disconnect cylinder according to previous instructions and record final weight. Replace valve protector and label cylinder.
- VI. Establish product take-off to designated storage tank (4C-4A, B, or C)
- A. Adjust pressure in designated tank to be equal or slightly less than pressure (PI-18) on overhead accumulator by adding N₂ if required or by venting.
 - B. Align valves to connect designated tank to overhead accumulator vent line. Make minor pressure adjustment if required.
 - C. Establish specified product take-off rate through FI-3A (design, 80 gph).
 - D. Continue removal of product until reboiler level is too low for efficient operation or reboiler temperature (TI-5-4) rises approximately 20°F. higher than top-of-column temperature (TI-5-2) indicating a build-up of high boiling impurities in the bottoms. Analysis of overhead product during early batches will help establish a maximum allowable temperature rise.
 - F. When product take-off is to be discontinued, close valve to FI-3A, and permit line to BCl₃ tank to drain. Shut down steam to reboiler, close valve to storage section at northeast corner of Step I structure and liquid and vapor block valves adjacent to storage tank.
- VII. Remove bottoms material, rich in high-boilers, if they occupy a significant portion of reboiler volume or if analysis indicates same. Distill as much as possible from the bottom, using a high reflux ratio (10/1) when it is necessary to remove heavy components from the pot.
- A. Connect weighed 100-pound cylinder to flexible hose on end of drain-to-decontamination line.

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- B. Open cylinder valve and evacuate cylinder through the QD provided.
- C. Note reboiler liquid level (4LG-5).
- D. Open the valve at the bottom of the drain line to fill the cylinder approximately 80%; do not completely fill cylinder since there would be danger of overpressurizing the cylinder by hydrostatic pressure after it had been valved off.
- E. After draining the short section of line from the process line block valve, close the cylinder valve and evacuate and N₂-purge the flexible hose, using the QD provided.
- F. Disconnect the cylinder, which is then ready for weighing and moving to the acid disposal scrubber.
- G. Cap the end of the flexible hose to prevent contamination of open end of hose.

SHUTDOWN

- I. Check that product take-off and steam control valves are closed as previously described, and that BCl₃ supply and disposal cylinders are disconnected.
- II. Admit N₂ to column as necessary to raise pressure to 20 psig.
- III. Turn off cooling water to condenser and valve in feed line adjacent to column for a prolonged shutdown.

RERUN OF PRODUCT IN TANKS (4C-4A, B, C) IF IMPURE

- I. Start cooling water to suction line cooler to pump (4G-2).
- II. Open the bottoms withdrawal line valve on the storage tank containing the material to be rerun. (Leave drain line valve closed.)
- III. Check that Step I feed line downstream of (4FI-7) to see that it is closed.
- IV. Open corresponding valve to column (4C-2A) between pump and column.
- V. Start feed to the column by starting the feed pump (4G-2). Since this pump is normally controlled by LIC-14, the pumping rate is set by a manual setting of that instrument.
- VI. The remainder of the rerun operation is similar to the normal procedure already described.

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EQUIPMENT

I. BCl_3 Distillation column (4C-2A).

A. Description

Column is carbon steel 8" dia. x 24' high, 21 ft. of which are packed with 1/2" Intalox saddles. The reboiler pot is approximately 35-1/2" dia. x 9' and will hold a normal BCl_3 charge of 3000 lbs. Steam coils in the reboiler operate on 40 psig steam. The overhead condenser (4E-2A) is a 10 ft. Grissum-Russell fintube with cooling water on the shell side and the process on the tube side.

B. Pressure Ratings

1. Design pressure - 225 psig at 250°F.

2. Relief devices

BD-2, 1-1/2" at 200 psig, backed up by PSV-1, 1-1/2" x 2" at 225 psig.

C. Feed Streams

1. Liquid BCl_3 from storage cylinder on weigh scale (4V-2).

2. (Alternate) Liquid BCl_3 from storage tanks (4C-4A, B, or C) for rerun.

D. Exit Streams

1. Liquid BCl_3 overhead to storage cylinder on weigh scale (4V-2) if impure, or to storage tanks (4C-4A, B, or C).

2. High boilers out bottom outlet to 100 lb. cylinder on intermittent basis.

E. Function

Produce a purified BCl_3 , low in phosgene and in high boilers, for use as a feed material to Step I.

F. Controls

1. Automatic - None.

2. Manual

a. Column pressure is maintained at desired level by hand venting overhead accumulator to destructive vent header.

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- b. Boil-up rate, as indicated on reflux flow indicator (FI-2A) and product flow indicates (FI-3 and 3A), is controlled by hand control valve on steam to reboiler.
- c. Reflux temperature can be controlled within limits by hand control valve on cooling water to condenser (4E-2A).
- d. Product take-off rate is controlled by hand valve.

3. Analytical

- a. Phosgene content of overhead, and therefore its acceptability as Step I feed material, is determined by IR analysis.
- b. Level of high boilers in overhead (and in bottoms for material balance purposes) is determined by IR and wet chemical methods.

G. Alarms - None

II. Purified BCl_3 Storage Tanks (4C-4A, B or C)

A. Description

Each tank is carbon steel, approximately 24" dia. x 9' high and holds approximately 175 gallons (2000 lbs.) of BCl_3 .

B. Pressure rating

- 1. Design pressure - 100 psig at 650°F.
- 2. Relief devices

BD-2, 4 and 5, 1-1/2" at 90 psig, backed up by PSV-3, 4 and 5, respectively, 1-1/2" x 3" at 100 psig.

C. Feed Stream - purified BCl_3 from distillation column (4C-2A).

D. Exit Streams

- 1. Purified BCl_3 to Step I via pump 4G-2.
- 2. (Alternate) Off-spec BCl_3 to distillation column (4C-2A) for rerun.

E. Function

Hold a supply of purified BCl_3 for Step I.

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F. Controls - None

G. Alarms - None

III. Purified BCl_3 charge pump (4G-2)

A. Description

Lapp Pulsafeeder, Type CFS-2. Capacity is 13.7 gph, at 75 rpm. SS diaphragm with teflon gasketing. Maximum allowable pressure is 600 psig. Cone-type check valves.

B. Design Operating Conditions

1. Flow 0.1 gpm (63.7 lbs./hr.).
2. Discharge pressure - 340 psig.

C. Relief Devices

1. External - None
2. Internal - 370 psig.

D. Suction - from BCl_3 storage tanks (4C-4A, B or C).

E. Discharge - to Step I (constitutes a portion of feed to reactor).

F. Function

Provide purified BCl_3 to Step I as required.

G. Special Features

1. Suction to pump is cooled in a double pipe heat exchanger to prevent cavitation in the pump.
2. Suction to pump goes through a Y strainer to eliminate particles which might interfere with cone checks in pump.

H. Controls - automatic.

Pumping rate is controlled by one LIC-14, the level controller on the HCl column (1C-5). Signal to the pump is recorded by R-8, and flow rate indicated by rotameter FI-7.

I. Alarms - None.

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IV. BCl_3 Weigh Scale (4V-2) and Cylinder Roller (4V-3)

A. Description

A Fairbanks-Morse Model 1206 simple beam scale with a capacity of 4000 lbs. Platform is equipped with rollers to facilitate the turning of the large BCl_3 cylinders placed on the scales.

B. Function

Provide an accurate measure of raw material (BCl_3) fed to Step IV and of phosgene-rich cut removed by distillation column (4C-2A).

C. Alarm

Low weight alarm (WAL-1) is tripped by scale beam and signals that cylinder on scale is nearly empty.

V. Hydrogen Supply System

A. Description

H_2 normally comes from a mobile (trailer) unit left at the unloading station by the supplier (Victor Equip. Co.). Facilities exist for accommodating two trailers, only one of which is used at a time. In addition, a reserve H_2 supply is maintained in a bank of 120 cylinders, also provided by the supplier. When a fresh trailer supply is connected up, it is used as necessary to pressure up the stationary bank by momentarily opening the regulator bypass. Trailers are considered empty at 50 psig.

B. Function

Provide a continuous 50 psig (nominal) H_2 supply to Step I and, if needed, a 275 psig supply to Step II.

C. Capacity

1. One trailer holds approximately 60,000 scf (70°F., 1 atm.).
2. The reserve bank holds 40,000 scf.

D. Relief Devices

1. Each cylinder is equipped with a fusible plug for relief in the event of it being involved in a fire.
2. The H_2 header is protected by PSV-7, 3/4" x 1" at 100 psig.

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E. Design Operating Conditions

1. H₂ header pressure - 50 psig nominal (275 psig for Step II).
2. H₂ flow rate - 3.3 lbs./hr. (10.3 scfm).
3. Temperature - Ambient.

F. Controls - Automatic.

1. Pressure - H₂ header pressure is maintained by pressure regulators, one for the trailer supply and one for the stationary bank. The former is set slightly higher than the latter so no H₂ flows from the bank until the connected trailer's pressure has dropped to the header pressure (50 psig nominal).
2. Excess Flow - Should the flow of hydrogen increase substantially as in the case of the serious leak, a signal from 4FR-6 closes the excess flow valve (EV-3) in the H₂ supply header. The valve must be manually reset in the open condition after the unusual condition is corrected.

G. Alarm

1. If excessive flow condition exists, alarm (FAH-3) sounds simultaneously with closing of excess flow valve (EV-3).
2. PAL-2 sounds alarm when trailer pressure reaches 100 psig so arrangements can be made to transfer to the second trailer. In general, operation off the stationary bank should be avoided if possible.

OPERATING PROCEDURES

Step V - Refrigeration

Operating Instructions

This system is designed to operate automatically. The compressors will cycle in relation to the refrigerating duty to be performed; the greater the load, the larger the running period and vice versa. Since operation is automatic, any change made to one part of the system may affect another part.

A. Third-Stage Compressor

To start up the third-stage, 100 h.p. Worthington compressor, proceed as follows:

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1. Close the disconnect switch on the magnetic stirrer.
2. Depress the reset button to "On" on the control transformer circuit breaker.
3. Push the starter switch for the third-stage unit.
4. The following controls are in operation at this time on the third-stage unit.
 - a. Time delay relay permits operation of compressor until oil pressure up to requirements. Low oil pressure after about 90 seconds will shut down complete refrigeration system.
 - b. Time delay relay opens all unloading solenoids on compressor. Unit starts off 25 per cent loaded. After approximately 60 seconds, relay closes and solenoids load compressor.
 - c. The unloading solenoids will now be operating at the following conditions:

	Solenoid No.		
	1	2	3
Capacity, unloaded	75%	50%	25%
Conditions, unloaded	8.0 psig -24°F.	4.0 psig -32°F.	0.0 psig -42°F.
Capacity, loaded	100%	75%	50%
Conditions, loaded	10.0 psig -20°F.	6.0 psig -28°F.	2.0 psig -37°F.

- d. Low water pressure switch on condenser water will shut down the system on low pressure. Water flow should be set for a rise of 8°F. under full load conditions.
 - e. Both high and low pressure cut-offs will shut down unit upon reaching set pressures. Restart is automatic on change of pressure in the opposite direction.
5. At all times, even when unit is shut down, the crankcase heater in the compressor is on thermostatic control.
6. Push "On" button on "Third-Stage Operation Only" switch after third-stage compressor has been running for about 10 minutes. This will permit operation of first and second-stage compressors.

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B. First and Second-Stage Compressors

To start up the first (7-1/2 h.p.) and second (10 h.p.) York rotary compressors, proceed as follows:

1. Close disconnect switches on magnetic starter for each compressor.
2. Push starter button for each unit.
3. The following controls are in operation at this time on both the first and second-stage compressors.
 - a. Normally closed relay timer to be open at start. A bypass solenoid on the compressor is then activated to permit start-up unloaded. Timer closes bypass solenoid after about 90 seconds.
 - b. Three-way solenoid valve controls cooling water to compressor jacket. With power on, the water goes through the jacket to sump drain. With power off, the water is shut off and the jacket drains.
 - c. Both high and low pressure cut-offs will shutdown unit. Restart is automatic on change of pressure in the opposite direction.
 - d. Low oil pressure will shut off unit.
 - e. A high temperature element in the case of the rotary compressor will shut down the unit if there is an inadequate cooling water flow.

C. Weekend Operation or System Pumpdown

The following procedure can be used to either maintain the system over a weekend or for pumpdown. Only the third-stage compressor is utilized for this service.

1. Push the "Off" button on the "Third-Stage Operation Only" switch. This switch will prevent operation of first and second-stage compressors and also shut off oil feed to these two units. For double safety, push the "Off" button on the starter switches for the second and first-stage compressors.
2. Push starter button for third-stage unit. The system is now on pumpdown operation and will pump the liquid refrigerant into the high side receivers and hold the entire low side at the pressure setting on the low pressure cut-out switch on the third stage.

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3. When the "Off" button on the "Third-Stage Operation Only" switch is activated, the following additional controls are shut off:
 - a. Level control for drain on minus 20°F. accumulator.
 - b. Sporlan level control on minus 20°F. accumulator.
 - c. Level control on minus 50°F. accumulator.
 - d. Solenoid on oil regenerator.
 - e. Solenoid on main liquid line out of high receiver.
Closing this valve prevents refrigerant from re-entering back into system.

D. Start-Up of Refrigerant Circulating Pump

The circulation of R-22 by means of pump 5G-1 provides the refrigerating medium for the minus 20 and minus 50 systems. To start up this system, proceed as follows:

1. Pump 5G-1 is off.
2. Open valve at bottom of vessel, 5C-2, and open pump bypass line 5R-48 - 3/8" - H back to vessel. Check pressure gauge in gas side of 5C-2. Pressure regulator 5PCV-7 must be holding pressure in vessel 4 psig lower than pressure in minus 20 accumulator. This reduced pressure permits flow of return refrigerant from minus 20 accumulator to pump tank 5C-2.
3. Fill vessel 5C-2 about 28" above LC-1 level control point. Fill by opening hand expansion valve in fill bypass line 5R7 - 5/8" - H. Check liquid level by noting frost line on outside of the pump bypass line. (Make tape mark on this line once best level to fill has been established.) Close hand expansion valve when proper liquid level is reached.
4. Start pump 5G-1 and circulate R-22 through exchangers on minus 20 and 50 systems. LC-1 control should now maintain proper level in pump vessel. If initial charge of liquid discharge from pump draws down liquid level in 5C-2 too far, the pump will start to cavitate. If LC-1 does not provide enough initial make-up, supplement by opening hand expansion valve on bypass (this is a temporary action only).

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APPENDIX K

Calculation Procedures - Diborane Pilot Plant
(Sample Calculations and Worksheets)

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Calculation Procedures for the Diborane Pilot Plant

1. % Conversion (from analysis of 1E-2E) discharge)

$$\% \text{ Conversion} = \frac{\text{mole \% BHCl}_2}{\text{mole \% BHCl}_2 + \text{mole \% BCl}_3} \times 100$$

2. H₂/BCl₃ Ratio (from analysis of 1E-2E discharge)

$$\text{Ratio} = \frac{100 - (\text{mole \% BHCl}_2 + \text{mole \% BCl}_3)}{\text{Mole \% BHCl}_2 + \text{mole \% BCl}_3}$$

3. BHCl₂ Produced (as lbs. B₂H₆)

- a. BCl₃ Feed to Reactor

$$\text{GPH (from 1 FRC-1)} \times \text{lbs. BCl}_3/\text{gal.} \times \text{time} = \text{lbs. BCl}_3 \text{ fed to reactor}$$

- b. Total BHCl₂ produced (as B₂H₆)

$$\text{lbs. BCl}_3 \text{ fed to reactor} \times \% \text{ conversion} \times \frac{27.7}{6 \times 82.75} = \text{lbs. BHCl}_2 \text{ (as B}_2\text{H}_6\text{)}$$

- c. Net BHCl₂ produced (as B₂H₆)

$$\text{Wt. \% BHCl}_2 \text{ in BCl}_3 \text{ feed (from 1C-5B analysis)} \times \text{lbs. BCl}_3 \text{ fed to reactor} = \text{lbs. BHCl}_2 \text{ fed to reactor}$$

$$(\text{Total BHCl}_2 \text{ produced} - \text{BHCl}_2 \text{ fed to reactor}) \times \frac{27.7}{6 \times 82.75}$$

$$= \text{net BHCl}_2 \text{ (as B}_2\text{H}_6\text{)}$$

4. HCl Recovered (as lbs. B₂H₆)

- a. lbs. HCl liquid in 1C-9 (from calibration curve of 1C-9)

- b. lbs. HCl vapor

$$\text{Volume of Vapor Space} = 34.3 - \frac{\text{lbs. HCl liquid}}{\text{Density of HCl in lb./gal.}}$$

$$\text{lbs. of HCl in Vapor} = \frac{3.4 \times \text{Pressure} \times \text{Volume of Vapor Space}}{\text{Temperature } ^\circ\text{R}}$$

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$$\begin{aligned} \text{c. Total HCl Recovered (as B}_2\text{H}_6) &= (\text{lbs. HCl liquid} + \text{lbs. HCl vapor}) \\ &\times \frac{27.7}{6 \times 36.5} \end{aligned}$$

5. B₂H₆ Recovered

- a. lbs. B₂H₆ liquid in 1C-7A & B (from calibration curve)
- b. lbs. B₂H₆ vapor

$$\text{Volume of Vapor Space} = 13.3 - \frac{\text{lbs. B}_2\text{H}_6 \text{ liquid}}{\text{Density in lbs./gal.}}$$

$$\text{lbs. B}_2\text{H}_6 \text{ vapor} = \frac{2.58 \times \text{pressure} \times \text{volume vapor space}}{\text{Temperature (}^\circ\text{R)} \times \text{Compressibility Factor}}$$

$$\text{c. Total B}_2\text{H}_6 = \text{lbs. B}_2\text{H}_6 \text{ liquid} + \text{lbs. B}_2\text{H}_6 \text{ vapor.}$$

6. Yields

- a. Based on BCl₃ make-up

$$\begin{aligned} \text{B}_2\text{H}_6 \quad \frac{\text{lbs. B}_2\text{H}_6 \text{ collected}}{27.7} \times \frac{2 \times 117.2}{\text{lbs. BCl}_3 \text{ added to system}} \times 100 \\ = \% \text{ yield} \end{aligned}$$

- b. Based on hydrogen make-up

$$\text{B}_2\text{H}_6 \quad \frac{\text{lbs. B}_2\text{H}_6 \text{ collected}}{27.7} \times \frac{6 \times \text{SCF/m H}_2}{\text{Total SCF added}} \times 100 = \% \text{ yield}$$

- c. Based on total BHCl₂ produced

$$\text{B}_2\text{H}_6 \quad \frac{\text{lbs. B}_2\text{H}_6 \text{ collected}}{\text{lbs. BHCl}_2 \text{ produced (as B}_2\text{H}_6)} \times 100 = \% \text{ yield}$$

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Calculation Work Sheet No. 1 (Sample)

Step I

% Conversion and H_2/BCl_3 Ratio
(Based on 1E-2E Analyses)

Run No. 7

Date	Time	1E-2E Analyses		% BCl_3 + % $BHCl_2$ Total	% $BHCl_2$ x 100 = Conv. Total	H_2/BCl_3 $\frac{100 - Total}{Total}$ = Ratio
		% BCl_3	% $BHCl_2$			
3/26					#1	#2
		No Samples - Assume 10% Conversion (low temp.)				
3/27	0845	20.4	4.85	25.25	19.2	2.96
	0945	23.2	6.46	29.66	21.8	2.37
	1055	34.2	7.05	41.25	17.1	1.42
	1300	28.7	7.40	36.1	20.5	1.77
3/28	0155	37.1	7.45	44.55	16.7	1.24
	0205	37.6	6.97	44.57	15.6	1.24
	0610	33.7	6.86	40.56	16.9	1.47
3/29	0300	37.7	3.98	41.68	9.5	1.40
	0600	39.1	5.83	44.93	13.0	1.23
	0910	37.4	5.08	42.48	12.0	1.35
3/30	0130	34.1	7.6	41.7	18.2	1.40
	0445	33.4	7.8	41.2	18.9	1.43
	0640	34.0	7.14	41.14	17.4	1.43
3/31	0610	28.6	7.53	36.1	20.9	1.77
	1145	29.9	6.77	36.7	18.4	1.72
	1505	30.4	7.27	37.7	19.3	1.65
					<u>1.58 Over-all</u>	

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Calculation Work Sheet No. 2 (Sample)
Step I, BHC₁₂ Production

Run No. 7

Date	Time	Δ t (hrs.)	BCl ₃ Feed (1 FRC-1)	BCl ₃ to Reactor (gal/M)	BCl ₃ to Reactor (lb./M)	BCl ₃ to Reactor (lbs.)	% Conv.	BHCl ₂ Produced (lbs.)	Produced (as lbs. B ₂ H ₆)	Total BHCl ₂ (as lbs. B ₂ H ₆)	BHCl ₂ Recycled (as lbs. B ₂ H ₆)	Net BHCl ₂ (as lbs. B ₂ H ₆)
3/26	1715	0	6	0	0	0	0	0	0	0	0	0
	1830	0.25	25	42.3	409.5	102.4	10	10.24	0.4	1.68	0.01	1.64
3/27	0700	11.0	35	67.2	650.5	7,155.5	10	715.55	28.19	32.83	0.73	32.00
	0800	1.0	6	0	0	0	0	0	0	32.83	0	32.00
	1030	1.0	24	40.3	390.1	390.1	21.8	85.0	3.35	38.93	0.05	38.01
3/28	1345	21.35	35	67.2	650.5	13,823.1	15.3	2,114.9	83.33	144.90	4.96	138.65
	2000	6.25	30	55.7	539.2	3,370.0	10.8	364.0	14.34	159.24	0.53	152.46
3/29	2000	24.0	35	67.2	650.5	15,612.0	11.5	1,795.4	70.74	229.98	2.89	220.31
3/31	2130	49.5	35	67.2	650.5	32,199.75	18.4	6,085.8	239.78	469.76	18.52	441.57
<u>Total</u>		<u>124.25</u>				<u>77,101.35</u>		<u>11,922.9</u>				
Reactor Total <u>123.25</u>												
Average Reactor Feed Rate				$\frac{77,101.35}{123.25}$	= 625.6 lbs./M.							
Average % Conversion				$\frac{11,922.9}{77,101.35} \times 100$	= 15.5%							
Average Temperature of BCl ₃ Feed to Reactor				= 160°F. - 9.96 lbs./gal. density.								

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Calculation Work Sheet No. 3 (Sample)
Step I, BHCl_2 Recycled
(Based on 1C-5B Analysis)

Run No. 7

Date	Time	BCl_3 Mole %	BHCl_2 Mole %	82.15 x Mole % BHCl_2	117.2 x Mole % BCl_3	Wt. BCl_3 + Wt. BHCl_2	Wt. % BHCl_2
3/26	2000	99.72	0.28	0.232	116.9	117.13	0.2
3/27	0225	99.63	0.37	0.306	116.8	117.11	0.26
	1834	99.66	0.34	0.281	116.8	117.08	0.24
	1740	99.44	0.56	0.463	116.5	116.96	0.40
3/29	0130	99.04	0.96	0.794	116.0	116.74	0.68
	0645	99.58	0.42	0.348	116.7	117.05	0.30
3/30	0305	96.20	3.8	3.145	112.7	115.85	2.71
	0950	99.09	0.91	0.753	116.1	116.9	0.64
3/31	0215	98.4	1.6	1.324	115.3	116.6	1.14
	1025	97.96	2.04	1.688	114.8	116.5	1.45

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Calculation Work Sheet No. 4 (Sample)
Step I, HCl Recovered (as B₂H₆)

Run No. 7

Date	Time	1C-9 Level (in.)	lbs. HCl Liquid	Δ Press. (psig)	Temp. (°R)	Vol. Vapor ft. ³	lbs. HCl Vapor	Total lbs. HCl	HCl (as lbs. B ₂ H ₆)
3/26	2100	3.2	0	0	456	34.3	0	0	0
3/27	0530	10.8	110	42	440	32.6	10.6	121	15
	1830	22.2	375	49	430	28.4	8.8	384	49
3/28	2050	39.9	790	73	429	21.8	12.6	803	102
3/29	0530	46.8	960	82	428	19.1	12.4	972	123
	2000	59.0	1240	115	430	14.6	13.3	1253	159
3/30	2100	3.7*	1790 + 0	21	428	34.3	5.7	1796	227
3/31	0530	16.2	1790 + 220	43	446	30.8	10.1	2020	256
	1330	25.4	1790 + 450	59	437	27.1	12.4	2252	285
		<u>Total 2395</u>							

*HCl in 1C-9 dumped.

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Calculation Work Sheet No. 5 (Sample)
Step I, B₂H₆ Recovery

Run No. 7

Date	Time	Storage Tsk Level (in.)	lbs. B ₂ H ₆ Liquid	Press. (psig)	Temp. (°R)	Vol. Vapor ft. ³	C Compres- sibility	lbs. B ₂ H ₆ Vapor	Total lbs. B ₂ H ₆
<u>1C-7A</u>				(170 psig)					
3/26	2100	1.5	0	0	517	13.3	-	0	0
3/27	0530	1.5	0	0	515	13.3	-	0	0
	1530	12.6	23	-55	428	12.2	0.84	-4.8	18.0
3/28	1320	21.2	55	-52	430	10.8	0.83	-4.1	51.0
3/29	0530	31.8	95	-21	418	8.9	0.81	-1.4	94.0
	1330	38.6	119	-6	419	7.8	0.79	-0.4	119.0
3/30	1415	53.4	173	+84	418	5.4	0.72	2.3	175.0
	2100	56.6	185	+91	421	4.8	0.70	3.8	189.0
3/31	0530	57.6	188.5	+7	418	4.7	0.78	0.3	189.0
	0330	61.8	205.5	+29	421	3.9	0.76	0.9	206.0
<u>1C-7B</u>									
3/31	0530	37.0	25.0	-75	376	8.1	0.88	-4.7	20.3
	2245	47.0	63.0	+39	397	6.4	0.77	2.1	64.0
<u>Total of 1C-7A & 7B</u>									
3/31	0530								209.3
	1130								239.0
	2245								273.0

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Calculation Work Sheet No. 6 (Sample)
Step I, BCl_3 + H_2 Consumption

Run No. 7

BCl_3

Start	4C-4A	75"	66°F.	133 gal.	x 11.15	1482.95
	4C-4B	95"	65°F.	170	x 11.2	1904.0
	4C-4C	89"	55°F.	159	x 11.25	<u>1788.75</u>
						<u>5175.7</u>
End	4C-4A	27"	59°F.	42	x 11.2	471.4
	4C-4B	56"	54°F.	97	x 11.2	1076.4
	4C-4C	37"	55°F.	62	x 11.17	<u>692.5</u>
						<u>2260.3</u>

Total BCl_3 Consumed $5175.7 - 2260.1 = \underline{2915.7 \text{ lbs.}}$

H_2

H_2 Trailer	670 psig	65°F.	= 66	from chart
	150 psig	52°F.	= <u>16</u>	
			50 x 255	= 12,750 scf
	1710 psig	43°F.	= 174	
	1160 psig	70°F.	= <u>114</u>	
			60 x 170	= 10,200 scf
Bank	1600	- 51	= 161.5	
	1300	- 52	= <u>132.0</u>	
			29.5	
	17.80	- 45	= 180.5	
	1675	54	<u>167.5</u>	
			13	(29.5+13.0) x 203.6 = 8,650
				Total H_2 = 31,600 scf

H_2 Consumption

Known H_2 leak through stuffing box of $1K-1$ = 0.5 scf/m
 $124.25 \times 60 = 7455$ minutes = 3,728 scf H_2 lost.
 $31,100 - 3,728 = 27,872$ scf H_2 consumed, say 27,900 scf.
 scf = 1 ft.³ at 1 atm. + 70°F.
 Vol/lb. mole = $359 \times \frac{530}{492} = 386$ scf/lb. mole

K-10

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Calculation Work Sheet No. 7 (Sample) Step I, Yields

Run No. 7

A. Based on BCl_3 Make-Up			
B_2H_6	$\frac{275}{27.7} \times \frac{2 \times 117.2}{2916}$	$\times 100$	= 79.2
HCl	$\frac{305}{27.7} \times \frac{2 \times 117.2}{2916}$	$\times 100$	= 88.6
B. Based on H_2 Make-Up			
B_2H_6	$\frac{273}{27.7} \times \frac{6 \times 386}{27,900}$	$\times 100$	= 81.8
HCl	$\frac{305}{27.7} \times \frac{6 \times 386}{27,900}$	$\times 100$	= 91.4
C. Based on Total BHCl_2 Produced			
B_2H_6	$\frac{273}{469.8}$	$\times 100$	= 58.1
D. Based on Net BHCl_2 Produced			
B_2H_6	$\frac{273}{441.6}$	$\times 100$	= 62.5

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APPENDIX L

Sampling Procedures and Analytical Methods -
Diborane Pilot Plant

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APPENDIX L

Sampling of Step I Liquid and Gas Streams

Procedure No. S-10

The procedures given here are those adhered to when sampling Step I liquid and gas streams. They must be followed closely if good samples are to be obtained. These streams may contain any or all of the following compounds: BCl_3 , BHCl_2 , HCl and B_2H_6 . All are injurious to the human system if inhaled or contacted with the skin. In addition, B_2H_6 and BHCl_2 can burn or explode on contact with air. Therefore, care and good judgment must be exercised in handling these samples. The sampling procedure must be followed carefully and suitable protective clothing must be worn. Protective clothing consists of coveralls, rubber shoes, gloves, safety glasses and hard hats. If BCl_3 or HCl fumes are present in the area where samples are to be taken, an air mask must be worn. If B_2H_6 leaks are evident in the area, notify the plant operators immediately and retire from the area until the difficulty is overcome. Do not attempt to sample in an area where the odor of B_2H_6 is present.

Apparatus

- A. Steel cylinders, 10 cc. vol. with double valved sub-chamber and "Hi-Seal" nut on end.
- B. Steel cylinders, 300 cc. vol., single valve with "Hi-Seal" nut on end.
- C. IR cells, 10 cm., metal body with Imperial "Hi-Seal" nut.
- D. IR cells, 10 cm., glass body with 10/30 std. taper male ground joint.

Procedures

A. Procedure for Sampling Step I Liquid Streams for IR Analysis

- 1. Take special 10 cc. cylinder and 5/8" wrench to sample point (Figure L-1).
- 2. Attach cylinder to sample point.
- 3. Blow out vacuum hose with N_2 .
- 4. Attach vacuum hose to sample point.
- 5. Turn on vacuum at station and check gauge to be sure vacuum is available.

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Procedure No. S-10 (cont.)

6. Check Kerotest valve - it must be closed.
7. Open both 1/4" valves on sample point.
8. Open both valves on sample cylinders.
9. Evacuate until all BCl_3 is removed from cylinder and sample point. This can be determined by holding hand on sample point; when no longer cold, the BCl_3 has evaporated.
10. Close 1/4" valve to vacuum system.
11. Open Kerotest valve about one turn.
12. Wait 15-20 seconds and close Kerotest valve.
13. Open 1/4" valve to vacuum system and evacuate until point ceases to be cold.
14. Close 1/4" valve to vacuum system.
15. Open Kerotest valve about one turn.
16. Wait 15-20 seconds and close Kerotest valve.
17. Close top valve on sample cylinder (one nearest cylinder proper).
18. Open 1/4" valve to vacuum system and evacuate until BCl_3 is removed from point. A N_2 purge and further evacuation is recommended.
19. Close bottom valve on sample cylinder (one nearest sample point).
20. Open top valve of sample cylinder. This provides cylinder with freeboard.
21. Close 1/4" valve to vacuum system.
22. Turn off vacuum at station.
23. Disconnect vacuum hose, blow out with N_2 and replace on rack.
24. Disconnect cylinder and place caps on sample point.
25. Return to laboratory and attach cylinder in an inverted position to suitable vacuum rack.
26. Attach glass-bodied IR cell to vacuum rack.

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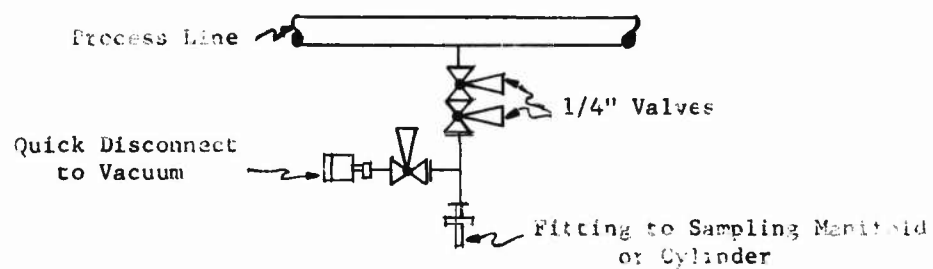


Figure L-1. Step I, Liquid Stream Sampling Assembly

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Procedure No. S-10 (cont.)

27. Attach a cold trap to the vacuum rack. This can be a 50 ml. centrifuge tube immersed in liquid N_2 .
28. Pump out entire system thoroughly and check for leaks.
29. If leak free, close stopcock to cold trap.
30. Close stopcock to vacuum pump.
31. Carefully open bottom valve of cylinder and let in sample to about 50 mm. pressure.
32. Close cylinder valve.
33. Open stopcock to cold trap and freeze down.
34. Pump off any non-condensables by opening stopcock to vacuum pump.
35. Close stopcocks to pump and cold trap.
36. Let in sample to desired pressure. The pressure used will depend upon the particular sample, but will generally be from 50 to 150 mm.
37. Read manometer and record pressure and temperature on work sheet.
38. Close stopcock to IR cell.
39. Open stopcock to cold trap.
40. Pump off non-condensables by opening stopcock to vacuum pump.
41. Close vacuum rack valve adjacent to IR cell.
42. Remove IR cell from vacuum rack. Sample is now ready for analysis by IR.

B. Procedure for Sampling Step I Gas
Streams for IR Analysis

1. Take 300 cc. steel cylinder and 5/8" wrench to sample point (Figure L-2).
2. Attach cylinder to sample point.
3. Blow out vacuum hose with N_2 .

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Procedure No. S-10 (cont.)

4. Attach vacuum hose to sample point.
5. Turn on vacuum at station and check gauge to be sure vacuum is available.
6. Check Kerotest valve - it must be closed.
7. Open the 1/4" valve on sample point.
8. Open valve on cylinder and evacuate.
9. Close 1/4" valve to vacuum system.
10. Open Kerotest valve carefully and let in about 10 lbs. of sample pressure.
11. Close Kerotest valve.
12. Open 1/4" valve to vacuum system and evacuate.
13. Repeat Steps 9 through 12 three more times to insure a good sample.
14. Close 1/4" valve to vacuum system.
15. Open Kerotest valve carefully and let in about 10 lbs. of sample pressure.
16. Close Kerotest valve.
17. Open valve on sample cylinder.
18. Open 1/4" valve to vacuum system. A N₂ purge and further evacuation is recommended.
19. Close 1/4" valves on sample point.
20. Turn off vacuum at station.
21. Disconnect hose, blow out with N₂ and return to rack.
22. Disconnect sample cylinder and replace caps on sample point.
23. Return to laboratory and attach cylinder to suitable vacuum rack.
24. Attach glass-bodied IR cell to vacuum rack.

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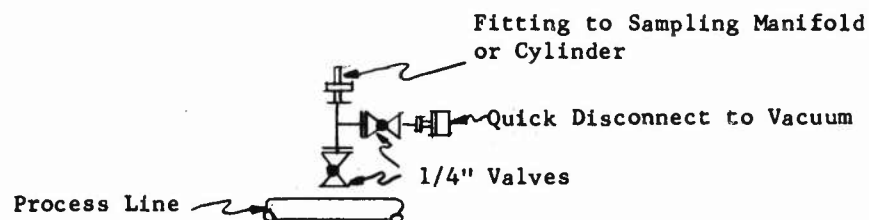


Figure L-2. Step I, Gas Stream Sampling Assembly

Procedure No. S-10 (cont.)

25. Attach a cold trap to the vacuum rack. This can be a 50 ml. centrifuge tube immersed in liquid N_2 .
26. Pump out entire system thoroughly and leak check.
27. If leak free, close stopcock to cold trap.
28. Close stopcock to the vacuum pump.
29. Carefully open cylinder valves and let in sample to a pressure of 50 to 100 mm.
30. Close cylinder valve.
31. Open stopcock to cold trap and freeze down condensables.
32. Open valve to vacuum pump and pump off non-condensables.
33. Close the stopcocks to pump and cold trap.
34. Let in sample to desired pressure. Generally a pressure of about 30 to 80 mm. is used. Pressure used will vary with the sample point.
35. Read manometer and record pressure and temperature.

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Procedure No. S-10 (cont.)

36. Close stopcock to IR cell.
37. Open stopcock to cold trap.
38. Pump off non-condensables.
39. Close vacuum rack valve adjacent to IR cell.
40. Remove IR cell from vacuum rack. Sample is now ready for IR analysis.

C. Procedure for Sampling Step I Reactor
Effluent (1E-2E) for IR Analysis

1. Take 10 cm. metal-bodied IR cell and two 5/8" wrenches to sample point (Figure L-3).
2. Attach cell to sample point.
3. Add liquid N₂ to trap and open valve on vacuum pump. This point has its own vacuum pump and trap system since the plant vacuum cannot always be relied upon to pull sufficient vacuum for a 100 mm. sample. This trap should be emptied daily during operation by attaching to plant vacuum and removing from liquid N₂; other end of tube is clamped off.
4. Open 1/4" valve on sample point.
5. Open valve on IR cell.
6. Pump out until manometer is level. This point has its own manometer for determining sample pressure.
7. Open Kerotest valve to vent system all the way. If gauge shows pressure increase in line when vent is opened, there is a plug in the vent line to the scrubber and engineers should be notified.
8. Turn on air in cooling coil.
9. Open sample flow valve all the way. The line gauge should show a positive pressure of about 4 lbs. at this point.
10. Let reactor effluent flow through vent for 3 minutes.
11. While effluent is flowing, check the sample point and IR cell for leaks by closing sample point valve leading to vacuum pump. If manometer remains flat for 2 minutes then system should be leak free.

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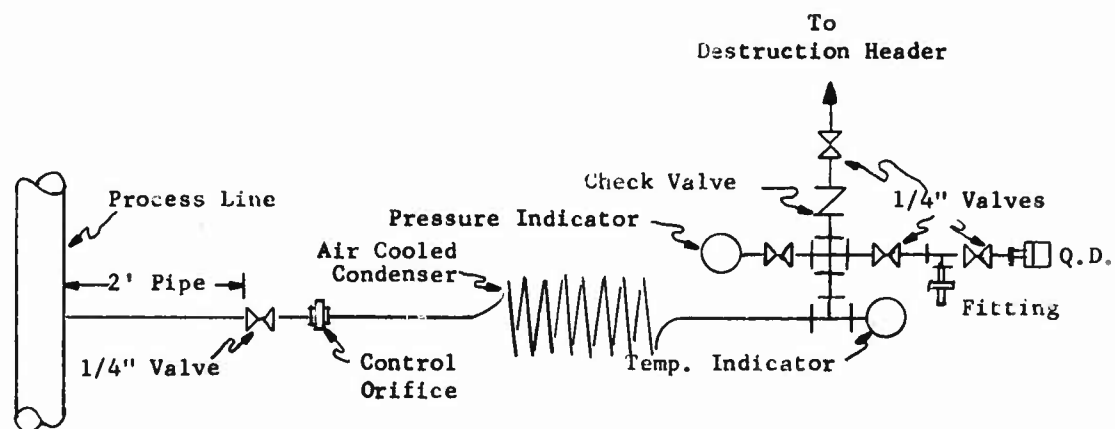


Figure L-3. Step I, Reactor Effluent Sampling Assembly

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Procedure No. S-10 (cont.)

12. Open valve to vacuum pump for another minute as a precautionary measure. It is essential that there be no air leaks into the system since even the slightest air leak leads to a loss of BHCl_2 values.
13. Close valve to vacuum pump.
14. Carefully let in about 100 mm. pressure by opening Kerotest valve leading to effluent flow.
15. Close Kerotest valve to effluent flow and pump out through cold trap.
16. Repeat this purge three more times.
17. Finally, let 70 to 90 mm. into IR cell, read pressure, and close cell valve. Also record temperature at sample point.
18. Pump remainder of sample out through trap.
19. Close valve to vacuum pump and valve on top of vacuum pump.
20. Turn off reactor effluent flow, cooling air and vent flow, in that order.
21. Disconnect sample cell and place cap on sample point.
22. Run sample on IR as soon as possible.

D. Procedure for Sampling Step I Gas
Streams for Hydrolysis

1. See Procedure B of this section and follow Steps 1 through 24.

E. Procedure for Sampling Step I Liquid
Streams for Hydrolysis

1. See Procedure A of this section and follow Steps 1 through 25.

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Analytical Methods

Determination of Total (Non-Volatile) Solids in Boron Trichloride

Procedure No. C-10

Method Application

This method applies to the determination of non-volatile materials which may accumulate in the APN Step I liquid process streams.

Equipment Required

1. Standard double valve, 10 ml., liquid sample cylinder.
2. Cone bottom tube, 50 ml. graduations, with stopcock and $\frac{1}{8}$ 10/30 male ground joint.
3. Suitable vacuum rack assembly.
4. Liquid transfer assembly, consisting of:
 - a. Tubing coupling, 1/4", Imperial "Hi-Seal," for sample cylinder attachment.
 - b. Three-way valve, with free passage through body and needle seat 90° to body passage.
 - c. Bottom connection, consisting of and terminating in $\frac{1}{8}$ 10/30 female ground joint, for attachment of cone bottom tube.
5. Dewar flasks and supply of liquid N₂.

Procedure

1. Liquid gas transfer equipment set-up:
 - a. Three-way valve positioned such that free passage is in vertical plane and needle seat outlet in horizontal plane.
 - b. Tubing coupling on top and bottom glass connection facing down.
 - c. Connect needle seat outlet to vacuum source (vacuum rack via tubing).
2. Weigh sample cylinder (full) on coarse balance to two decimal places. Record on Work Sheet (D-1).

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Procedure No. C-10 (cont.)

3. Weigh cone bottom tube (clean, dry and evacuated) on analytical balance to four decimal places. Record on Work Sheet (D-1).
4. Fasten cylinder (in inverted position) to tubing coupling on top of liquid gas transfer assembly.
5. Connect cone bottom tube (upright vertical position) to ground joint on bottom of transfer assembly.
6. Evacuate assembly, cone tube and cylinder manifold (to primary cylinder valve) through assembly needle valve seat.
7. Cool cone bottom tube in liquid N₂ bath.
8. Close assembly needle valve.
9. Open cylinder primary valve and allow contents to drain into cone bottom tube and freeze.
 - a. Draining should be done carefully and slowly.
 - b. After major portion drained, allow several minutes to completely empty cylinder (primary valve wide open).
10. Close cylinder valve and stopcock on cone tube.
11. Evacuate assembly body and remove cylinder.
12. Reweigh empty and evacuated cylinder on coarse balance to two decimal places.
 - a. Record weight on Work Sheet (D-1) and calculate weight of liquid transferred.
13. Remove cone tube from assembly and attach to appropriate place on vacuum rack for distillation of volatile components.
 - a. Carefully distill volatile components from cone tube to another tube or trap for disposal. Avoid bumping or moderating distillation with dry-ice slush.
 - b. For disposal of distillate, see Notes.
 - c. Finish distillation by warming tube with hot water until remaining contents appear stationary.
14. Remove cone tube from vacuum rack, dry well, and reweigh analytically to four decimal places.

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Procedure No. C-10 (cont.)

- a. Record weight on Work Sheet (D-1) and calculate weight of non-volatile solids.
15. Solids in tube may be removed and saved for further investigation by solvent or aqueous extraction (acid or alkaline solution).

Calculations

$$\text{Non-Volatiles (\% wt.)} = \frac{\text{Wt. solids, cone tube}}{\text{Wt. liquid gas, cylinder}} \times 100$$

Operational Notes

1. Where stream samples contain diborane or dichloroborane, extreme care must be taken to avoid leaks in system or any contact with air or moisture. Solvents such as acetone are also to be avoided.
2. Distillation must be performed carefully to avoid loss of solids by entrainment.
3. Disposal of distillate must be made carefully into a good water aspirator system. Such a system is available in the Decaborane Compound.
4. In cleaning or extracting solids from cone bottom tube, after non-volatile analysis, liquid should be carefully drawn into tube (excluding air) with a cooling bath available should the contents react violently.

Care in this operation is important due to possible residual boranes.
Use safety shield for personal protection.

Hydrolysis of Boron Trichloride

Procedure No. C-11

Boron trichloride is hydrolyzed to form boric acid and hydrochloric acid. This is the first step in the determination of boron, chloride, silicon, and chlorine in boron trichloride.

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Procedure No. C-11 (cont.)

Apparatus

1. Cone bottom tube, 50 ml. graduations, with stopcock and $\frac{T}{S}$ 10/30 male ground joint.
2. Suitable vacuum rack assembly.
3. Liquid gas transfer assembly consisting of:
 - a. Tubing coupling, 1/4", Imperial "Hi-Seal," for sample cylinder attachment.
 - b. Three-way valves with free passage through body and needle seat 90° to body passage.
 - c. Bottom connection, consisting of and terminating in $\frac{T}{S}$ 10/30 female ground joint, for attachment of cone bottom tube.
4. Dewar flasks.

Reagents

1. Distilled water.
2. Liquid N₂.

Procedure

1. Obtain sample as per Sampling Procedure No. S-10 (E).
2. Clean, evacuate and weigh centrifuge tube.
3. Weigh to four decimal places using analytical balance.
4. Attach centrifuge tube to vacuum system and chill tube in liquid N₂.
5. Transfer about 5 ml. of sample to the tube using the gas liquid transfer assembly.
6. Slowly warm sample until it is slightly below room temperature.
7. Quickly weigh sample.
8. Freeze sample in liquid N₂.

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Procedure No. C-11 (cont.)

9. Add about 20 ml. of distilled water very slowly; too rapid addition of water may lead to loss of material. Use a $\frac{1}{8}$ 10/30 outer joint.
10. Remove from liquid N_2 and place in beaker of ice water.
11. When hydrolysis seems to be complete, remove from ice water and allow to warm to room temperature.
12. Dilute hydrolyzed mixture to 250 ml. volume with distilled water. If large samples are used, it may be necessary to add NaOH to get the boric acid into solution.
13. Sample is now ready for colorimetric and chemical analyses.

Determination of Silicon in Boron Trichloride

Procedure No. C-12

Silicon is determined in boron trichloride by colorimetry using the silico-molybdic acid method.

Apparatus

1. Beckman Model "B" Spectrophotometer.
2. Color cells, glass, 1 cm. light path.
3. Volumetric flasks, 100 ml., and other standard laboratory items.

Reagents

1. Hydrochloric acid, Reagent, 1:1 volume dilution.
2. Ammonium hydroxide, Reagent, 28% (15 M).
3. Acetic acid, Reagent, glacial.
4. 2,4-dinitrophenol indicator, prepared as follows:
 - a. Dissolve 100 gms. ammonium molybdate, Reagent crystal, in 400 ml. of distilled water and 80 ml. of 15 M ammonium hydroxide. Filter if necessary and store in plastic bottle labelled Solution 1.

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Procedure No. C-12 (cont.)

- b. Mix 400 ml. of 16 M nitric acid (conc.), Reagent, and 600 ml. of distilled water. Store in plastic bottle and label Solution 2.
- c. To prepare reagent solution for use in silicon analysis, mix one volume of Solution 1 carefully into two volumes of Solution 2. The mixed solution is good for a day or two; hence, it should be prepared in small quantities and stored in plastic.

Procedure

1. Pipette a 25 ml. aliquot of the hydrolyzed BCl_3 sample, from the 250 ml. solution, and place in a 100 ml. volumetric flask.
2. Dilute to approximately 50 ml.
3. Prepare a separate 100 ml. volumetric flask for a blank.
 - a. Add all of the reagents used in the sample flask, particularly the ammonium hydroxide, in the same volumes or quantities.
4. Add 1 ml. of 2,4-dinitrophenol indicator.
5. Add concentrated ammonium hydroxide dropwise, while swirling, until the solution assumes a yellow color.
6. Wash down the neck of the flask with distilled water and add 1:1 HCl dropwise until the yellow color just disappears.
7. Add 1 ml. of glacial acetic acid and 5 ml. of the prepared ammonium molybdate solution.
8. Dilute to mark volume and mix thoroughly.
9. After 15 minutes, read absorbancy of the solution on the spectrophotometer, at 420 millimicrons, with the reagent blank set at zero absorbancy.
10. Convert the absorbance reading to the silicon concentration (ppm) by using one of the following formulae:

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Procedure No. C-12 (cont.)

Calculations

$$\text{Silicon (ppm)} = \frac{250 \times 100 / \text{aliquot (ml.)} \times \text{Si in color soln. (ppm)}}{\text{Sample weight (gms.)}}$$

or

$$\frac{250 \times 100 / 25 \times K \times A}{\text{Sample weight (gms.)}}$$

$$A = kc \quad K = 1/k$$

$$C = KA$$

$$K = C/A = 20.15 \text{ (from curve)}$$

$$\text{Silicon (ppm)} = 26,300 \times \frac{A}{\text{Sample wt. (gms.)}}$$

Determination of Chlorine in Boron Trichloride

Procedure No. C-13

Chlorine is determined in boron trichloride by colorimetry using o-tolidine as indicator.

Apparatus

1. Beckman Model B Spectrophotometer.
2. Two 100 ml. volumetric flasks.
3. 25 ml. pipette, 2 ml. pipette.

Reagents

O-tolidine solution (0.744 g/l), distilled water, 1:1 hydrochloric acid.

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Procedure No. C-13 (cont.)

Procedure

1. Pipette a 25 ml. aliquot of the hydrolyzed sample of boron trichloride into a 100 ml. volumetric flask.
2. Dilute to 40 ml. with distilled water.
3. Add 40 ml. of 1:1 hydrochloric acid.
4. In a separate 100 ml. volumetric flask, prepare a blank by adding 40 ml. of 1:1 hydrochloric acid to 40 ml. of distilled water.
5. Add 2.0 ml. of o-tolidine reagent to each flask.
6. Dilute both the sample and blank to the mark with distilled water and mix well.
7. Allow solutions to stand for nine minutes for color development.
8. Using a wavelength setting of 438 millimicrons on the Beckman Model B Spectrophotometer, place the blank in the light path.
9. Adjust the absorbance reading to zero (% T = 100).
10. Place sample in light path and read absorbance.
11. Determine concentration of chlorine in the color solution by referring to calibration curve.
12. Calculate concentration of chlorine in original sample as follows:

$$\text{Conc. of chlorine (ppm)} = 1000 \times \frac{\text{Cl in color soln. (ppm)}}{\text{Wt. of Sample}}$$

or

$$\text{Conc. of chlorine (ppm)} =$$

$$\frac{\text{Sample dilution} \times \frac{100 \text{ (ml.)}}{\text{(250 ml)}} \times \text{Cl in color soln. (ppm)}}{\text{Weight of sample (gms.)}}$$

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Analysis of Boron Trichloride - Wet Methods

Procedure No. C-14

General

The weighed, hydrolyzed, and diluted sample of boron trichloride is analyzed for boron and chloride content by alkali and silver nitrate titrations, respectively, of aliquot portions of the diluted solution (250 ml).

From the total boron, chloride, and original weight of BCl_3 (prior to hydrolysis), the per cent (wt.) of BCl_3 , the chloride to boron ratio (Cl/B), and the per cent (wt.) of free hydrogen chloride (HCl) can be calculated.

A. Total Boron Analysis

Reagents

Standard sodium hydroxide solution, 0.1 N
Standard acid solution, 0.1 N
Mannitol, powder, A.R.
Distilled water

Apparatus

pH meter
Pipettes
Burettes
Mannitol scoop
Titration vessel (400-600 ml. beaker)
Magnetic stirrer and bar

Procedure

1. Pipette a 25 ml. aliquot of diluted solution (250 ml.) into a 400-600 ml. beaker and add distilled water to a volume of about 200 ml.
2. Place beaker in titration position and insert pH electrodes and stirrer bar.
3. Adjust pH with acid or alkali to a pH of 6.0.
4. Add one scoop of mannitol (ca. 5 gms.) to the stirred solution.
5. Titrate with standard sodium hydroxide solution (0.1 N) to a pH of 8.0. The volume of alkali is used in the calibration of total boron.

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Procedure No. C-14 (cont.)

6. A blank determination should be made without the solution aliquot, and the last alkali volume corrected by subtracting blank alkali volume.

Calculations

$$\text{Total Boron (gms.)} = (\text{ml. NaOH soln.})(N)(0.1082)$$

B. Total Chloride Analysis (Volhardt Method)

Reagents

Standard silver nitrate solution, 0.1 N
Potassium thiocyanate solution, 0.1 N
Nitrobenzene, A.R.
Ferric alum solution (ca. 5%)
Nitric acid, A.R., concentrated
Distilled water

Apparatus

Burettes
Pipettes
Erlenmeyer flasks, 250 ml.

Procedure

1. Pipette a 25 ml. aliquot of diluted solution (250 ml.) into a 250 ml. volumetric flask and bring to volume. From this pipette a 25 ml. aliquot into a 500 ml. Erlenmeyer flask.
2. Add ca. 50 ml. of distilled water, 5 ml. concentrated nitric acid, and 50.0 ml. of standard silver nitrate solution (0.1 N).
3. Agitate solution by swirling and add 2 ml. nitrobenzene and 2 ml. ferric alum solution. Swirl until precipitate is wetted with nitrobenzene.
4. Backtitrate with potassium thiocyanate solution (0.1 N) until the appearance of the first persistent red color (ca. 30 sec. persistency).
5. A blank determination should be made without the solution aliquot and the silver solution volume corrected.

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Procedure No. C-14 (cont.)

Calculations

$$\text{Total chloride (gms.)} = \frac{[(\text{ml. AgNO}_3)(N) - (\text{ml. KCNS})(N)] (3.546)}{\text{Volume aliquot (ml.)}}$$

Analytical Data Via Calculation

$$\text{Boron Trichloride: } \text{BCl}_3 (\% \text{ wt.}) = \frac{(\text{gms. total boron})(10.82)(100)}{\text{wt. BCl}_3 \text{ hydrolyzed (gms.)}}$$

$$\text{Ratio Cl/B: } \text{Ratio Cl/B} = \frac{(0.3054)(\text{gms. total chloride})}{\text{Total boron (gms.)}}$$

Hydrogen Chloride:

1. Total chloride (gms.) in sample.
2. Chloride (gms.) as BCl_3 = $(9.822)(\text{total boron, gms.})$.
3. Chloride (gms.) as HCl , Item 1 - Item 2.

$$\text{HCl (gms.)} = (1.028)(\text{Item 3}).$$

$$\text{HCl (\% wt.)} = \frac{(\text{gms. HCl})(100)}{\text{Wt. BCl}_3 \text{ (gms.)}}$$

Vacuum-Hydrolysis Analysis of AFN Step I Streams

Procedure No. C-15

General

The vacuum-hydrolysis apparatus presents a means of analyzing AFN Step I stream samples, in gas or liquid form, for the following chemical components: non-condensable vapors (H_2 , materials having vapor pressure at liquid N_2 temperature, -195°C); boron trichloride, dichloroborane and diborane (by IR analysis); dichloroborane or diborane (by hydrolysis followed by measurement of evolved H_2); boron trichloride and hydrogen chloride (by wet boron and chloride analysis after correction for boron and chloride equivalents of other borane components).

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Procedure No. C-15 (cont.)

Equipment

A. The fixed or stationary components of the vacuum-hydrolysis apparatus are:

1. A high vacuum manifold (see Figure L-4) with following attachments:
 - a. Mechanical vacuum pump (Cenco HYVAC-7 or equal).
 - b. Mercury diffusion pump and heater (Delmar DS-7050).
 - c. Concentric type glass vapor trap and isolation stopcocks.
 - d. N₂ drying column (P₂O₅), bottom valve and top stopcock.
 - e. Single scale McLeod gauge (Delmar DS-7090).
 - f. Glass tubing lines and stopcocks to volume systems.
2. A coarse vacuum manifold with following attachments:
 - a. Mechanical vacuum pump (Cenco HYVAC-7 or equal).
 - b. Trap assembly for waste sample collection:
 - (1) Metal turning filled trap (ca. 500 ml. capacity).
 - (2) Concentric type trap for waste removal.
 - (3) Chemical traps (SiO₂ gel) for pump protection.
 - c. Mercury manometer ("U" type, 0-760 mm. Hg.).
 - d. Glass tubing lines and stopcocks to volume systems.
3. Two glass analytical systems, each consisting of:
 - a. Sample introduction point (common to both systems).
 - b. Calibrated sample volume (SV-1 or SV-2).
 - (1) Mercury manometer ("U" type, 0-760 mm. Hg.).
 - (2) Thermometer (°C) for sample temperature.
 - (3) Stopcocks and connections for IR gas samples.
 - (4) Stopcock and glass tubing to gas condensation system.
 - c. Gas condensing system consisting of:
 - (1) Glass spiral condensation trap.
 - (2) Mercury manometer ("U" type, 0-760 mm. Hg.).
 - (3) Manifold with stopcocks for connection of gas hydrolysis flasks.
 - (4) Stopcock and glass tubing to Toepler pump.
 - d. Automatic Toepler Pump (Delmar-Urry DS-7030-100), 1000 cc., piston stroke.
 - (1) Relay control box (Delmar DS-7031).
 - (2) Vacuum line, solenoid valve and gas ballast tank.
 - (3) Mechanical vacuum pump (Cenco HYVAC-7 or equal).
 - (4) Stopcock and glass tubing to gas measuring system.

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Procedure No. C-15 (cont.)

- e. Gas measuring system, consisting of:
 - (1) Three calibrated glass volumes interconnected for four volume combinations (Volumes HV-1, HV-2 and HV-3, or HV-4, HV-5 and HV-6).
 - (2) Mercury manometer ("U" type, 0-760 mm. Hg.) calibrated for mercury displacement in left arm.
 - (3) Thermometers ($^{\circ}\text{C}$) for gas temperature.
- 4. Utility services to vacuum-hydrolysis apparatus:
 - a. Electricity, 120 v., A.C., 60 cycles, outlets on ends of support rack.
 - b. Vacuum line, water aspirator, for operation of McLeod gauge.
 - c. N_2 line to drying column and opposite end of support rack.
 - d. Oxygen line to each end of support rack.
 - e. Cooling water line and return for Mercury diffusion pump.
- B. The mobile or non-stationary components of the vacuum-hydrolysis apparatus are:
 - 1. Sample collection cylinders or bombs (see Sampling Techniques, Step I).
 - 2. Infrared gas cells, 10 cm. gas path.
 - 3. Cone bottom tubes, ca. 50 ml. graduated capacity.
 - 4. Hydrolysis flasks, tube bottom, ca. 1100 ml. capacity, ground joint and stopcock on top.

Equipment Applications

The vacuum-hydrolysis apparatus can be used to analyze liquid and gaseous Step I stream samples for the following components:

- 1. Boron trichloride, liquid, for:
 - a. Phosgene and carbon tetrachloride, infrared.
 - b. Chlorine and silicon tetrachloride, hydrolysis-colorimetric.
 - c. Boron, chloride, BCl_3 and HCl , hydrolysis-wet methods.
- 2. Process stream samples, liquid and gas, for:
 - a. BCl_3 , BHCl_2 , and B_2H_6 , infrared.

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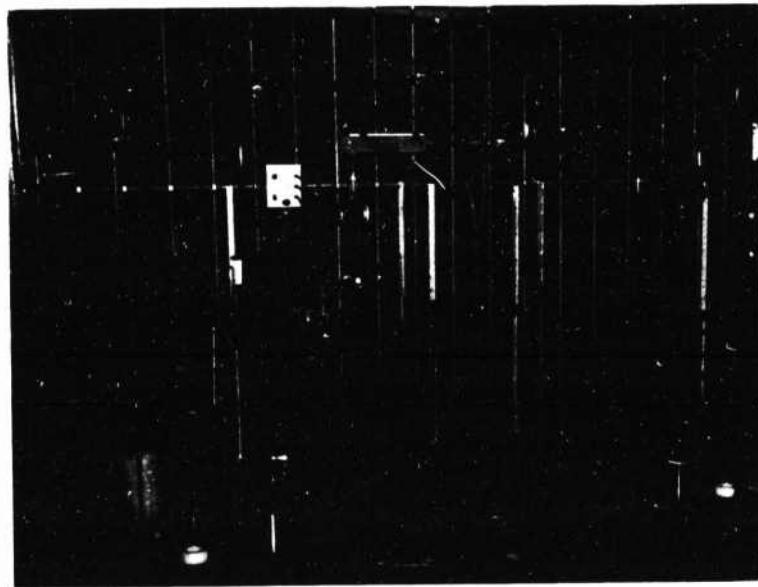


Figure L-4. Vacuum-Hydrolysis Apparatus

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Procedure No. C-15 (cont.)

- b. BHCl_2 or B_2H_6 , hydrolysis-hydrogen evolution.
 - c. Non-condensable gas (H_2), pressure measurement.
 - d. BCl_3 and HCl , hydrolysis-wet methods.
3. Reactor feed gas for:
 - a. Molar ratio of non-condensable to condensable.
Pressure measurements.
 4. Other process samples involving:
 - a. Vacuum manipulations and volume transfers.
 - b. Gas freeze-outs and hydrolysis.
 - c. Pressure measurements.
 - d. Partial sample removal and adjustment for IR analysis.
 - e. Mole content measurement by use of calibrated volumes.

Generalized Procedure

This procedure outline is intended to give a working description of the types of operations that this apparatus will handle. It does not describe the turning of each stopcock nor does it eliminate the need for thought and alertness on the part of the operator.

1. Evacuate all parts of the system, by means of the fine (high) vacuum manifold, to as low a pressure as can be reasonably obtained.
2. Close all stopcocks and watch manometers for signs of leakage. Correct situation (Shift Chemist) if necessary.
3. Attach sample cylinder or bomb to the centrally located sample manifold and evacuate to the primary cylinder valve.
 - a. Invert cylinders containing liquid samples such that only the liquid phase is sampled.
 - b. Gaseous samples may be taken into the system from upright cylinder.
4. Attach other sampling devices to appropriate position in system and evacuate.
 - a. IR cell to lower connection of sample volume (SV-1,2).
 - b. Cone bottom tube or hydrolysis flask to position on the manifold in the gas condensing portion of the system.

When tube or flask contains water or any other volatile material it must be frozen, at the temperature of liquid nitrogen (-195°C), before evacuating. Do not allow water or water vapor to enter the system.

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Procedure No. C-15 (cont.)

5. Close all stopcocks not necessary for introduction of sample into volume (SV-1 or SV-2).
6. Introduce sample into sample measuring volume (SV-1 or SV-2).
 - a. Adjust pressure to that satisfactory for IR sample and then close stopcocks connecting IR cell to volume. Record pressure on Work Sheets (A) or (F).
 - b. Raise sample pressure in volume to that satisfactory for other determinations.
 - (1) For samples containing principally BCl₃, do not exceed ca. 370 mm. Hg.
 - (2) For B₂H₆ samples do not exceed 100 mm. Hg.
7. Close stopcock connecting sample measuring volume and sample introduction manifold. Close cylinder valve, if not closed previously.
8. Measure pressure and temperature of sample volume and record on Work Sheets (E) or (I).

Close stopcock leading to manometer; tubing connected is not part of calibrated volume.

9. Immerse spiral gas condensing trap in liquid N₂ and slowly open trap to gas contents of sample volume.

Better gas collection is obtained if only the bulb of the trap is cooled and then the liquid N₂ level raised after the major part of condensation has taken place.

10. The pressure remaining in the sample volume and gas condensing system, as measured by the gas condensing system manometer, is due to non-condensable gases (H₂ and perhaps some N₂). These are then pumped into the gas measuring system by means of the Toepler pump.

Contents of spiral trap must be frozen well; do not permit any material condensable at liquid nitrogen temperature (-195°C) to enter the Toepler pump.

11. Carefully open stopcocks to Toepler pump and start automatic operation of pump. If a high non-condensable pressure exists on gas condensing side of Toepler pump, the mercury seal discharge valve of the pump will be violently opened and may be damaged. Gas flow can be controlled by use of the stopcock downstream from the spiral trap.

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Procedure No. C-15 (cont.)

12. The first calibrated gas measuring volume that the pump discharges into is HV-1 or HV-4.
 - a. The maximum discharge pressure that the pump will operate at is ca. 200 mg. Hg. If this pressure is reached before the gas condensing manometer shows no pressure, open the next gas measuring volume (HV-3 or HV-6).
 - b. If more volume is needed, HV-2 or HV-5 are available.
 - c. Operator must exercise judgment in selection of gas measuring volume combinations based on gas laws and knowledge of initial pressure on gas condensing side of pump.
13. When pressure in gas condensing system is zero, stop Toepler pump on down stroke and close stopcock on suction side.
 - a. Measure pressure and temperature of gas measuring system and record on Work Sheets (E) or (I).
 - b. Record the volumes used (cc.) on Work Sheets (E) or (I) and include volume due to displacement of mercury in left arm of manometer.
 - c. Calculate mole per cent non-condensables, Work Sheets (E) and (H).
14. Close stopcock connecting sample volume (SV-1 or SV-2).
15. Transfer condensables frozen in spiral trap to:
 - a. Cone bottom tube, in liquid N₂ bath, for BCl₃ analysis, Work Sheets (B) and (C).
 - b. Hydrolysis flask, containing 25 ml. of 0.1 N NaOH solution frozen in liquid N₂ bath, for BHCl₂ analysis by H₂ evolution and for wet analysis, Work Sheets (G) and (H).
16. Remove tube or flask from system and process as follows:
 - a. Process cone bottom tube containing BCl₃ as described in procedure for analysis of BCl₃. Weight of BCl₃ obtained from special case formula, Work Sheet (E).
 - b. Hydrolysis flask is allowed to warm to room temperature and stand for a period of time; to be determined by experience. If IR analysis showed that the sample contained no B₂H₆ mixed with BHCl₂, the flask can be returned to the vacuum system for determination of BHCl₂ content by H₂ evolution. See Work Sheet (G).

If sample contains both B₂H₆ and BHCl₂, the IR analytical values, Work Sheet (F), are used to calculate boron and chloride equivalent values for these components. See Work Sheet (G).

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Procedure No. C-15 (cont.)

17. Determination of BHC1_2 by H_2 evolution.

- a. Hydrolysis flask is returned to connection on gas condensing system and the volume between stopcocks evacuated.
- b. The hydrolyzed solution is refrozen with liquid N_2 and the flask examined for droplets of solution. If these are present, time must be taken to allow them to migrate to frozen zone. Warming spot with hand helps.
- c. Flask is opened to gas condensing system and Toepler pump started.
- d. Gas is pumped into gas measuring system, as previously described, until gas condensing system manometer shows zero pressure.
- e. Toepler pump is stopped on down stroke and connecting stopcocks closed.
- f. The pressure, temperature and volumes of gas collected in gas measuring system are recorded on Work Sheet (G), including displacement of manometer.
- g. Calculate mole per cent BHC1_2 , Work Sheet (G).

18. Wet analysis of hydrolyzed sample in hydrolysis flask.

- a. Remove hydrolysis flask and contents from vacuum system.
- b. Allow solution to thaw and return to room temperature.
- c. Remove cap from flask and quantitatively transfer solution to 250 ml. volumetric flask. Dilute to volume with distilled water. Aliquot portions of solution to be analyzed for boron and chloride values; see Work Sheet (H).
- d. Dry lower part of hydrolysis flask in oven in preparation for next use.

19. Preparation of vacuum-hydrolysis apparatus for next use:

- a. Evacuate contents of gas measuring system into coarse vacuum manifold, by-passing waste sample trap assembly. Finish evacuation of gas measuring system using high vacuum manifold.
- b. Remove remains of sample from sample introduction manifold, tubing connections and sample volume (SV-1 or SV-2) manometer by use of coarse vacuum manifold and waste sample trap. Finish evacuation of systems using high vacuum manifold.
- c. Evacuate entire vacuum assembly to best vacuum obtainable with high vacuum manifold.

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Procedure No. C-15 (cont.)

Operational Notes and Precautions

1. Provisions are made for introduction of dry nitrogen into the high vacuum manifold at the head of the concentric type trap. Nitrogen is dried by passing over P_2O_5 in a drying column.

2. Extreme care must be taken to prevent BCl_3 or boranes from entering the vacuum pumps. BCl_3 reacts rapidly with pump oil to produce HCl and sludge. Pump oil (with exception of pump servicing Toepler manifold) must be changed at least once a week (sooner if fumes are detected at pump vent). Pump oil levels should be checked once a day.

3. Instructions in operation and care of the Toepler pumps and McLeod gauge will be given by supervisor.

Adjustments in apparatus should be made only by shift chemist and only if situation warrants a change.

4. Waste sample trap should be maintained at dry ice-acetone bath temperature ($-78^\circ C$) and contents emptied on day shift.

5. Apparatus glassware and operating platform should be kept as clean and clear as possible.

6. Water flow to mercury diffusion pump must be on at all times that pump is in operation.

7. Only Kel-F No. 90 grease is to be used as a lubricant for stopcocks and ground joints.

8. In the event of breakage to a part of the system, every effort should be made to isolate the broken area to prevent damage to other parts of the system.

System Volumes and Calibration Data

1. Sample volume, SV-1 = 1066.6 cc.
2. Sample volume, SV-2 = 1035.2 cc.
3. Gas measuring volume, HV-1 = 108 cc.
4. Gas measuring volume, HV-2 = 2690 cc.
5. Gas measuring volume, HV-3 = 1091 cc.
6. Gas measuring volume, HV-4 = 93.3 cc.
7. Gas measuring volume, HV-5 = 2695 cc.
8. Gas measuring volume, HV-6 = 1026 cc.
9. Mercury manometer displacement (left arm) = 0.5 cc. per cm. Hg.

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Determination of HCl in B₂H₆ Product Streams
by Modified Vacuum Hydrolysis

Procedure No. C-16

This procedure is considerably faster than the standard vacuum hydrolysis (Procedure No. C-15) but it is lacking in that percentage non-condensables cannot be determined. It is used primarily for analyzing B₂H₆ product samples for HCl content.

Apparatus

1. High vacuum manifold with manometer.
2. Mechanical vacuum pump (Cenco HYVAC-7 or equal).
3. Mercury diffusion pump and heater.
4. Hydrolysis flasks, tube bottom, ground joint and stopcock on top. Known volume (ca. 1100 ml.).
5. Cone bottom tubes, ca. 50 ml. graduated capacity.
6. IR gas cells, 10 cm. gas path.
7. Thermometer located on vacuum rack.

Reagents

1. Isopropyl alcohol, Reagent grade.
2. Sodium hydroxide, approximately 0.1 N.
3. Silver nitrate, standard solution, approximately 0.1 N.
4. Potassium thiocyanate, standard solution, approximately 0.1 N.
5. Nitrobenzene, Reagent grade.
6. Ferric alum indicator, 10% solution.
7. Nitric acid, concentrated, A-R.

Procedure

1. Obtain sample. Follow Step I Sampling Procedure No. S-10 (D).
2. Attach IR gas cell to vacuum rack.
3. Attach hydrolysis flask to vacuum rack.

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Procedure C-16 (cont.)

4. Attach cone bottom tube to vacuum rack.
5. Pump out entire system thoroughly.
6. Check for leaks by closing stopcock to vacuum pump and waiting 3 minutes. The manometer should not change. If a leak is detected, do not proceed until it is located and corrected.
7. Immerse cone bottom tube in liquid N₂.
8. Close stopcocks to vacuum pump, cold trap and hydrolysis bulb.
9. Open sample cylinder valve and slowly let about 30-40 mm. B₂H₆ into IR cell.
10. Close sample cylinder valve.
11. Open stopcock to cold trap.
12. When manometer ceases to move, open stopcock to vacuum pump and evacuate non-condensables.
13. Open stopcock to hydrolysis flask.
14. Close stopcock to cold trap.
15. Close stopcock to vacuum pump.
16. Open sample cylinder valve slowly and let about 40 mm. pressure into IR cell and hydrolysis flask.
17. Close sample cylinder valve and read pressure exactly.
18. Record pressure on Work Sheet (F).
19. Close IR cell stopcock.
20. Open sample cylinder valve and let sample into hydrolysis flask to a pressure of about 100 mm.
21. Close sample cylinder valve.
22. Read pressure and temperature and record on Work Sheet (E-1).
23. Close stopcock to hydrolysis flask.
24. Open stopcock to cold trap and freeze down sample remaining in lines.
25. Run IR on sample as per Procedure No. IR-10. (page L-36).

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Procedure No. C-16 (cont.)

26. Take hydrolysis flask from rack and place tube bottom in liquid N_2 .
27. Slide ground glass $\frac{T}{S}$ 14/35 outer joint over standard taper stopcock.
28. Add about 25 ml. of a 50-50 mixture of Reagent grade isopropyl alcohol and 0.1 N NaOH to the outer joint.
29. Open stopcock to hydrolysis flask slightly and allow reagent to trickle in until reagent level in outer joint is just above stopcock.
30. Close stopcock and add another 25 ml.
31. Again open stopcock slightly and allow reagent to trickle in until level is again just above stopcock.
32. Close stopcock.
33. Remove hydrolysis flask from liquid N_2 and place in rack.
34. Finish IR analysis while hydrolysis flask is warming up.
35. When hydrolysis flask has reached room temperature, swirl contents until all signs of gas evolution cease.
36. Quantitatively transfer contents to a 500 ml. Erlenmeyer flask.
37. Add about 5 ml. of conc. HNO_3 .
38. Add $AgNO_3$ in excess with swirling.
39. Add about 5 ml. of nitrobenzene.
40. Add about 5 drops of ferric alum indicator.
41. Swirl about one minute.
42. Add KCNS to the first persistent light brown color. The color should last about 30 seconds.
43. Record milliliters $AgNO_3$ and KCNS used, and normalities on Work Sheet (E-1).
44. Calculate mole per cent HCl using Work Sheet (E-1).

Start-Up, Operation and Shutdown Procedures for Beckman IR-4Procedure No. I-30A. Instrument Start-Up1. Main Power

- a. Verify that main power switch is "on".
- b. Verify that glower is operating by observation of glower current meter or visual check. If glower is not on, turn operation selector switch to "start" until meter gives a reading. If glower will not start, have glower or glower heater replaced.

2. Rotating Mirrors

- a. Turn glower; adjust control clockwise to start rotating mirrors.
- b. Adjust glower current to 0.6 amp.

3. Drift Check

- a. Turn operation selector switch to "DB".
- b. Set slit program on "Std".
- c. Set gain at 6 per cent.
- d. Set period switch to 2.
- e. Block sample and reference beam paths with opaque shutters and position pen at mid-scale.
- f. If recorder pen drifts appreciably, adjust balance control until it ceases to drift.

B. Double Beam Operation

1. Set gain at 1.5
2. Set slit program at 2 X std.
3. Set scanning speed at one micron per minute.
4. Set trimmer comb control so pen reads about 100% with nothing in either light path.
5. With wavelength drive disconnect disengaged, set wavelength to desired value (usually 15 μ).
6. Place sample cell in instrument holder.
7. Engage wavelength drive disconnect.
8. Push start button.
9. Scan sample over desired wavelength region (usually entire range of 1-15 μ).

C. Instrument Shutdown

1. Turn operation selector switch to "SB".
2. Turn coarse gain to "1".

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Procedure No. I-30 (cont.)

3. Turn fine gain to 0.00.
4. Turn period control switch to "32".
5. When pen has returned to base line, turn glower adjust counterclockwise to shut off rotating mirrors.
6. Place pen in pen storage box.
7. Cover instrument with plastic cover.

Infrared Determination of Boron Trichloride, Dichloroborane, Diborane
Phosgene and Carbon Tetrachloride in Step I and Step IV Streams

Procedure No. IR-10

This method is based on the absorption of infrared energy by the compounds being determined.

Apparatus

Beckman IR-4 Infrared Spectrophotometer and 10 cm. IR gas cells.

Procedure

1. See IR-4 Start-Up Procedure No. I-30 (A).
2. See Step I Sampling Procedure No. S-10.
3. Place sample cell in IR-4 sample holder.
4. Write date, time, sample number, sample point, and mm. pressure on chart.
5. With wavelength and pen both set at 15 microns, press scan button and scan at one micron per minute.
6. When scan is completed, raise pen from paper and tear off chart with tear bar.
7. Place chart on large clip board for calculations.
8. For each peak used, draw a straight line across the base of the peak and a vertical line through the peak so that it intersects the base line.
9. Calculate absorbance from $A = \log \frac{I_B}{I_P}$ where I_B is the % transmittance of the base line where it intersects the vertical line and I_P is % transmittance of the peak.

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Procedure No. IR-10 (cont.)

10. Calculate mole % from mole % = $\frac{100 \cdot KA}{P}$ where K is a constant dependent upon wavelength and component being analyzed. A is absorbance and P is pressure of mm. of mercury. See Work Sheets (A) and (F) for K values.
11. Dispose of sample by freezing down into a cold trap and then running through a water aspirator.
12. Replace IR cell in desiccator for storage.

Infrared Determination of Hydrogen Chloride in Boron Trichloride

Procedure No. IR-11

This method can be applied to determining approximate HCl values in Step I liquid and gas streams. The two HCl peaks at 3.38 and 3.55 microns are quite weak and results are not too accurate, especially for small concentrations.

Apparatus

Beckman IR-4 Infrared Spectrophotometer
10 cm. IR gas cells

Procedure

1. See IR-4 Start-Up Procedure No. I-30 (A).
2. See Step I Sampling Procedure No. S-10. Instead of the usual 50-100 ml. sample pressure, 200-400 mm. is introduced into the IR cell.
3. Place sample cell in IR-4 sample holder.
4. Write date, time, sample number, sample point, and mm. pressure on chart.
5. With wavelength and pen both set at 15 microns, press scan button and scan at one micron per minute.
6. When scan is completed, raise pen from paper and tear off chart with tear bar.
7. Place chart on large clipboard for calculation.

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Procedure No. IR-11 (cont.)

8. Draw a straight line across the base of the peak and a vertical line through the peak so that it intersects the base line.
9. Calculate absorbance from $A = \log \frac{I_B}{I_P}$ where I_B is the % transmittance of the base line where it intersects the vertical line and I_P is the % transmittance of the peak.
10. Calculate mole % from mole % = $\frac{100 \cdot KA}{P}$ where K is a constant dependent upon wavelength and component being analyzed, A is absorbance and P is pressure in mm. of mercury. See Work Sheet (F-1) for K values.
11. Dispose of sample by freezing down into a cold trap and then running through a water aspirator.
12. Replace IR cell in desiccator for storage.

Determination of Boron, Chloride, NaOH
and pH of Scrubber Samples

Procedure No. MC-30

This procedure applies to samples taken from the plant scrubber or any other similar samples.

Apparatus

pH meter
Magnetic stirrer with stirring bars
Burettes and standard glassware

Reagents

1. Nitric acid, conc., A.R.
2. Sodium hydroxide, std. soln., approximately 0.1 N.
3. Silver nitrate, std. soln., approximately 0.1 N.
4. Potassium thiocyanate, std. soln., approximately 0.1 N.
5. Mannitol, reagent grade.

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Procedure MC-30 (cont.)

6. Nitrobenzene, reagent grade.
7. Ferric alum indicator, 10%
8. Sulfuric acid, std. soln., approximately 0.1 N.

A. Procedure for Determining Grams Per Liter Boron

1. Check pH meter daily against standard solution and adjust if necessary.
2. Pipette a suitable aliquot (usually about 10-25 ml.) into a 400 ml. beaker.
3. Add about 200 ml. distilled water.
4. Using a pH meter, adjust pH to 6.0 with NaOH and/or H₂SO₄ contained in burettes near pH meter. Agitation is by magnetic stirrer.
5. Add about 10 grams of mannitol.
6. When dissolved, titrate with std. NaOH to a pH of 8.0.
7. Add about one gram more of mannitol. If no appreciable change in pH occurs, titration is complete.
8. Record ml. NaOH on Work Sheet (D) and calculate g/l boron.

$$\text{Boron (g/l)} = \frac{(\text{ml. NaOH})(N)(10.83)}{(\text{ml. sample})}$$

B. Procedure for Determining Grams Per Liter Chloride

1. Pipette a suitable aliquot (usually 1-2 ml.) into a 500 ml. Erlenmeyer flask.
2. Add about 100 ml. distilled water.
3. Add about 5 ml. concentrated HNO₃.
4. Add AgNO₃ until precipitation of AgCl seems complete and then add 5-10 ml. excess.
5. Add about 5 ml. of nitrobenzene.
6. Add about 10 drops of ferric alum indicator.
7. Swirl until AgCl is well coated with nitrobenzene.

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Procedure MC-30 (cont.)

8. Add KCNS until first persistent light brown color is achieved. Contents of flask must be swirled vigorously during KCNS titration.
9. Record ml. of AgNO_3 and KCNS used on Work Sheet (D) and calculate g/l chloride.

$$\text{Chloride (g/l)} = \frac{[\text{ml. AgNO}_3(\text{N}) - (\text{ml. KCNS})(\text{N})] (35.46)}{(\text{ml. sample})}$$

C. Procedure for Determining Grams Per Liter NaOH

1. Pipette a 10 ml. aliquot into a 400 ml. beaker.
2. Add about 150 ml. distilled water.
3. Using a pH meter and magnetic stirrer, titrate with standard H_2SO_4 to a pH of 7.0.
4. Record ml. H_2SO_4 used on Work Sheet (D) and calculate g/l NaOH.

$$\text{NaOH (g/l)} = \frac{(\text{ml. H}_2\text{SO}_4)(\text{N})(40.0)}{\text{Sample Vol. (ml.)}}$$

D. Procedure for Determining pH of Solution

1. After boron, chloride and NaOH values have been obtained, pour remainder of sample into a 400 ml. beaker.
2. Immerse pH meter electrodes to a depth of about 3/4 inch in the solution.
3. Swirl contents of beaker gently about 10 seconds.
4. Depress "read" button and continue swirling.
5. Read and record pH value on Work Sheet (D).

Note: The pH meter should be checked at least once a day against a standard solution and adjusted if necessary.

WORK SHEET (A)

Analysis of Boron Trichloride

Date: _____ Time: _____ Sample NO: _____

Sample Designation: _____

Infrared Analysis:

Sample Pressure:

Temperature (t): _____ °C

Manometer (Right): _____ cm

Manometer (Left) : _____ cm

_____ cm x 10 = _____ mm Hg

Analysis, Phosgene:

λ	K
11.77	3.22
5.42	7.19

Wavelength (λ): _____ microns

Absorbance (A) = $\log \frac{I_B}{I_P}$ = $\log$ _____ = _____

Mole % = $\frac{K \times A \times 100}{\text{Sample Pressure (mm Hg)}}$ = _____ = _____

Analysis, Carbon Tetrachloride:

K = 1.60

Wavelength (λ): 12.56 microns

Absorbance (A) = $\log \frac{I_B}{I_P}$ = $\log$ _____ = _____

Mole % = $\frac{K \times A \times 100}{\text{Sample Pressure (mm Hg)}}$ = _____ = _____

Remarks: _____

Analyst(s): _____

WORK SHEET (B)

ANALYSIS OF BORON TRICHLORIDE

Date: _____ Time: _____ Sample No: _____

Sample Designation: _____

Sample Preparation:

Wt. sample tube + BCl₃ _____ g. Volume BCl₃ at -78°C _____ ml.
Wt. sample tube (tare) _____ g.
Wt. BCl₃ _____ g. *

Hydrolyze BCl₃, wash solution from tube and dilute to 250 ml. This is solution
for wet and colorimetric analyses.

Colorimetric Analysis:

Silicon:

Wave length () : 420 millimicrons

Silicon (ppm) = $26,300 \frac{\text{Absorbance}}{\text{Wt. BCl}_3 *}$

= 26,300 _____ = _____

Chlorine:

Wave length () : 438 millimicrons

Use absorbance value to obtain chlorine concentration (ppm) in color developed
solution from curve.

Chlorine (ppm) = $1000 \frac{\text{Cl}_2 \text{ in color soln. (ppm)}}{\text{Wt. BCl}_3 *}$

= 1000 _____ = _____

Remarks: _____

Analyst (s) _____

WORK SHEET (C)

Analysis of Boron Trichloride

Date: _____ Time: _____ Sample No. _____

Sample Designation: _____

Sample Preparation:

See work sheet (b) for weight of BCl_3 in 250 ml. solution. All analyses on this sheet are made on aliquot portions of this solution.

Wet Analyses

Boron

$$\begin{aligned} \text{Boron (g.)} &= \frac{(\text{ml. NaOH soln.})(N)(2.707)}{\text{Volume aliquot (ml.)}} \\ &= \frac{\quad (2.707) \quad}{\quad} = \quad ** \end{aligned}$$

Chloride

$$\begin{aligned} \text{Chloride (g.)} &= \frac{[(\text{ml. AgNO}_3)(N) - (\text{ml. KCNS})(N)] (8.865)}{\text{Volume aliquot (ml.)}} \\ &= \frac{\quad (8.865) \quad}{\quad} = \quad \end{aligned}$$

BCl_3

$$\begin{aligned} \text{BCl}_3 (\%) &= \frac{(\text{g. Boron } **)(10.82)(100)}{\text{Wt. BCl}_3^*} \\ &= \frac{\quad (1082) \quad}{\quad} = \quad \end{aligned}$$

Ratio Cl/B

$$\text{Ratio Cl/B} = \frac{(0.3054)(\text{g. Chloride})}{(\text{g. Boron } **)} = \frac{(0.3054)}{\quad} = \quad$$

Hydrogen Chloride

1	Chloride (g) in sample	_____
2	Chloride (g) as BCl_3 (9.822)(g. Boron)	_____
3	Chloride (g) as HCl 1 - 2 =	_____

$$\text{HCl (g.)} = (1.028)(3) = \underline{\hspace{2cm}}$$

$$\text{HCl (\%)} = \frac{(\text{g. HCl})(100)}{\text{Wt. BCl}_3^*} = \frac{\quad (100) \quad}{\quad} = \underline{\hspace{2cm}}$$

Remarks _____

Analyst(s) _____

WORK SHEET (D)

Analysis of Miscellaneous System Samples

Date: _____ Time: _____ Sample No.: _____

Sample Designation: _____

General Analyses:

Iron (Colorimetric):

Wavelength (λ) = 510 millimicrons K = 0.508

Iron (mg/100 ml) = 0.508 (Absorbance) = _____

Iron (gpl) = $\frac{K \times A}{\text{Aliquot (ml.)}}$ = _____ = _____

Boron (Titration):

Boron (gpl) = $\frac{(\text{ml. NaOH})(N)(10.83)}{\text{Sample Vol. (ml.)}}$ = _____ = _____

pH (solution) = _____

Chloride (Titration):

Chloride (gpl) = $\frac{[(\text{ml AgNO}_3)(N) - (\text{ml KSCN})(N)] (35.46)}{\text{Sample Vol. (ml)}}$ = _____

NaOH (Titration):

NaOH (gpl) = $\frac{(\text{ml H}_2\text{SO}_4)(N)(40.0)}{\text{Sample Vol. (ml)}}$ = _____ = _____

Other Analyses (Show Calculations):

Remarks: _____

Analyst(s): _____

WORK SHEET (D-1)

Determination of Total Non-Volatile Solids in Boron Trichloride

Date: _____ Time: _____ Sample No: _____

Sample Designation: _____

Wt. of Sample Cylinder + Sample . . . = _____ g

Wt. of Sample Cylinder after Transfer = _____ g

Wt. of Sample = _____ g ①

Wt. of Cone Bottom Tube + Solids . . = _____ g

Wt. of Cone Bottom Tube Empty . . . = _____ g

Wt. of Solids = _____ g ②

$$\text{Wt. \% Solids} = \frac{\text{②}}{\text{①}} 100 = \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$$

WORK SHEET (E)

Vacuum - Hydrolysis Analysis - Step I

Date: _____ Time: _____ Sample No: _____

Sample Designation: _____

Infrared Analysis:

Use Work Sheet (F), Boron Trichloride Stream Analysis - Step I

Sample Preparation: Temperature (t): _____ °C

Manometer (right): _____ cm
Monometer (left): _____ cm
 Δ _____ cm x 10 = _____ mm Hg

Special Case: For samples containing only BCl_3 and using volume SV-1:
$$\text{Wt. BCl}_3 \text{ (g.)} = \frac{1.988 \text{ (mm Hg)}}{t \text{ (}^\circ\text{C)} + 273.2} = \text{_____} = \text{_____} *$$

Moles of sample = $\frac{V(\text{mm Hg}/760)}{(82.06)(t^\circ\text{C} + 273.2)}$ = _____ = _____

Noncondensable Analysis: Temperature (t): _____ °C

Manometer (right): _____ cm
Manometer (left): _____ cm
 Δ _____ cm x 10 = _____ mm Hg

Manometer displacement (left): _____ cm x 0.5 = _____ cc

Volume total: _____ + _____ + _____ + _____ = _____ cc

Moles noncondensable = $\frac{V(\text{mm Hg}/760)}{(82.06)(t^\circ\text{C} + 273.2)}$ = _____ = _____

Mole (%) noncondensable = $\frac{\text{Moles noncondensable}}{\text{Moles of Sample}} \times 100 = \text{_____}$

Remarks: _____

Analyst(s): _____

WORK SHEET (E-1)

Determination of HCl in

B₂H₆ Product Streams by Vacuum Hydrolysis

Date: _____ Time: _____ Sample No.: _____

Sample Designation: _____

Volume of Hydrolysis Bulb = _____ ml (V)

Sample pressure = _____ mm (P) Temp. = _____ °C + 273.2 = _____ °K (T)

Moles of Sample = $\frac{(V) 760}{(82.06) (T)}$ = _____ = _____ (1)

Sample is run on IR for BHCl₂, BCl₃ and B₂H₆ (Work Sheet "F")

Chloride (g) due to BHCl₂ = (1) (mole % BHCl₂) * (70.92) = _____ (2)

Chloride (g) due to BCl₃ = (1) (mole % BCl₃) * (106.38) = _____ (3)

* Values obtained by IR (Work Sheet F) and expressed as decimal equivalents.

Wet Analysis for Total Chloride:

ml AgNO₃ used _____ ml (4) Normality AgNO₃ _____ N (5)

ml KSCN used _____ ml (6) Normality KSCN _____ N (7)

Chloride (g) = $\sqrt{(4) (5) - (6) (7)}$ (0.03546) = _____ = _____ (8)

Mole % HCl = $\frac{(8) - (2) - (3)}{(1)}$ (2.819) = _____ = _____

Remarks: _____

Analyst(s): _____

WORK SHEET (F)

Boron Trichloride Stream Analysis - Step I

Date: _____ Time: _____ Sample No: _____

Sample Designation: _____

Infrared Analysis:

Sample Pressure:

Manometer (Right): _____ cm.

Manometer (Left): _____ cm.

Temperature Correction:

_____ cm. x 10 = _____ mm Hg (P_L)

$$P_L = \frac{T_L \times P_P}{T_P}$$

$$T \text{ in } ^\circ K = t \text{ } ^\circ C + 273.2$$

P = plant

L = laboratory

Boron Trichloride:

λ	K
5.22	444
10.06	4.37

Wavelength (λ) = _____ microns

$$\text{Absorbance (A)} = \log \frac{I_B}{I_P} = \log \text{_____} = \text{_____}$$

$$\text{Mole (\%)} = \frac{K \times A \times 100}{P_L} = \text{_____} = \text{_____}$$

Dichloroborane

λ	K
9.12	7.46

Wavelength (λ) = _____ microns

$$\text{Absorbance (A)} = \log \frac{I_B}{I_P} = \log \text{_____} = \text{_____}$$

$$\text{Mole (\%)} = \frac{K \times A \times 100}{P_L} = \text{_____} = \text{_____}$$

Diborane

λ	K
5.32	160
6.23	12.9
8.48	39.8

Wavelength (λ) = _____ microns

$$\text{Absorbance (A)} = \log \frac{I_B}{I_P} = \log \text{_____} = \text{_____}$$

$$\text{Mole (\%)} = \frac{K \times A \times 100}{P_L} = \text{_____} = \text{_____}$$

Wt. % B_2O_3 in BCl_3

λ	K
7.22	43.7

$$\text{Absorbance (A)} = \log \frac{I_B}{I_P} = \log \text{_____} = \text{_____}$$

$$\text{Wt. \% } B_2O_3 \text{ in } BCl_3 = \frac{(K)(A)}{(BCl_3 \text{ Pressure})}$$

Remarks: _____

Analysts: _____

WORK SHEET (F-1)

Infrared Determination of Hydrogen Chloride

Date: _____ Time: _____ Sample No.: _____

Sample Designation: _____

Sample Pressure

Temperature (t) _____ °C

Manometer (Right) _____ mm

Manometer (Left) _____ mm

Pressure _____ mm (Hg)

Analysis of Hydrogen Chloride

λ K

Wavelength (λ) 3.38

3.38 1665

Absorbance (A) = $\log \frac{I_B}{I_P}$ = $\log$ _____ = _____

Mole % HCl = $\frac{K \times A \times 100}{\text{Sample Press.}}$ = _____ x _____ = _____

Enter results on Work Sheet (H) and indicate IR analysis

Remarks _____

Analyst(s) _____

WORK SHEET (G)

Vacuum-Hydrolysis Analysis - Step I

Date: _____ Time: _____ Sample No.: _____

Sample Designation: _____

Condensable Analysis:

Moles of sample (Work Sheet "E") = _____ ①

Dichloroborane by hydrolysis and hydrogen evolution:

Manometer (Right): _____ cm. Temperature (t): _____ °C

Manometer (Left): _____ cm.

_____ cm. x 10 = _____ mm. Hg

Manometer displacement (Left): _____ cm. x 0.5 = _____ cc.

Volume total: _____ + _____ + _____ + _____ = _____ cc.

Moles $H_2 = BHCl_2 = V \left[\frac{\text{mm. Hg}}{760} \right] = \frac{\text{_____}}{(82.06)(t + 273.2)}$

Mole % $BHCl_2 = \frac{\text{Moles } H_2}{\text{①}} = \frac{\text{_____}}{\text{_____}}$

Wt. $BHCl_2$ (g.) = Moles $BHCl_2$ x 82.76 = _____

Chloride (g.) due to $BHCl_2$ = Wt. $BHCl_2$ x 0.857 = _____ ③

Boron (g.) due to $BHCl_2$ = Wt. $BHCl_2$ x 0.131 = _____ ②

Corrections for the presence of Diborane:

If infrared analysis (Work Sheet "F") shows the presence of diborane, the following calculations must be used to obtain the boron and chloride equivalents of $BHCl_2$ and B_2H_6 .

Boron (g.) due to $BHCl_2$ = ① (Mole % $BHCl_2$)(0.1083) = _____ 2A

Chloride (g.) due to $BHCl_2$ = ① (Mole % $BHCl_2$)(0.7092) = _____ 3A

Boron (g.) due to B_2H_6 = ① (Mole % B_2H_6)(0.2166) = _____ ④

Remarks: _____

Analyst(s) _____

WORK SHEET (H)

Vacuum-Hydrolysis Analysis - Step I

Date: _____ Time: _____ Sample No.: _____

Condensable Analysis Continued:

Moles of sample (Work Sheet "E") = _____ 1

Wet Analyses; Total Boron and Chloride Values:

Solution in Hydrolysis flask diluted to 250 ml.

All wet analyses made on aliquot portions of this solution.

Boron (g.) = $\frac{(\text{ml. NaOH})(N)(2.707)}{\text{Aliquot (ml.)}}$ = _____ = _____ 5

Chloride (g.) = $\frac{[(\text{ml. AgNO}_3)(N) - (\text{ml. KCNS})(N)](8.865)}{\text{Aliquot (ml.)}}$ = _____ = _____ 6

Calculations:

See alternate values (Work Sheet "G") when both BHC1_2 and B_2H_6 are present in the same sample

Mole % BCl_3 = $\frac{[(5) - ((2) \text{ or } (2A)) - (4)](9.240)}{(1)}$ = _____ = _____

Chloride (g.) due to BCl_3 = $[(5) - ((2) \text{ or } (2A)) - (4)](9.823)$ = _____ (7)

Mole % HCl = $\frac{[(6) - ((3) \text{ or } (3A)) - (7)](2.819)}{(1)}$ = _____ = _____

Mole % non-condensables (Work Sheet "E") _____

Mole % Diborane (Work Sheet "F") _____

Mole % Dichloroborane (Work Sheets "F" or "G") (_____) _____

Mole % (other components, Work Sheet "D") (_____) _____

Mole % HCl (by IR Analysis, Work Sheet "F-1") _____

Mole % Total _____

Remarks: _____

Analyst(s) _____

WORK SHEET (I)

Analysis of Reactor Feed Gases - Step I

Date: _____ Time: _____ Sample No. _____

Sample Designation: _____

Infrared Analysis:

Use Work Sheet (F), BCl_3 Stream Analysis - Step I

Vacuum Analysis:

Sample Volume (SV-1 or SV-2) = _____ cc

Manometer (Right): _____ cm. Temperature (t): _____ °C

Manometer (Left): _____ cm.
_____ cm. x 10 = _____ mm. Hg.

$$\text{Moles of Sample} = \frac{V \left[\frac{\text{mm Hg}}{760} \right]}{(82.06)(t + 273.2)} = \text{_____} = \text{_____} \text{ (1)}$$

Noncondensables (as Hydrogen):

Manometer (Right): _____ cm. Temperature (t): _____ °C

Manometer (Left): _____ cm.
_____ cm x 10 = _____ mm. Hg.

Manometer displacement (Left): _____ cm. x 0.5 = _____ cc.

Volume total: _____ + _____ + _____ + _____ = _____ cc.

$$\text{Moles noncondensable} = \frac{V \left[\frac{\text{mm. Hg.}}{760} \right]}{(82.06)(t + 273.2)} = \text{_____} = \text{_____} \text{ (2)}$$

Condensables (as Boron Trichloride):

$$\text{Moles condensable} = \text{(1)} - \text{(2)} = \text{_____} = \text{_____} \text{ (3)}$$

Molar Ratio:

$$\text{Hydrogen/Boron Trichloride} = \frac{\text{(2)}}{\text{(3)}} = \text{_____} = \text{_____}$$

Wet Analyses:

For wet analysis of condensables use Work Sheet (H)

Remarks: _____

Analyst(s) _____

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Defense Technical Information Center
Attn: Ms. Kelly Akers (DTIC-R)
8725 John J. Kingman Rd, Suite 0944
Ft Belvoir VA 22060-6218

Dear Ms. Akers

This concerns Technical Report AD336009, Final Report for High Energy Fuels Project Volume III. Process Development for Diborane Production, June 1962. This record was previously "UNCLASSIFIED / LIMITED."

Subsequent to WPAFB FOIA Control Number 2012-01297-F, this record has been cleared for public release by Air Force Research Lab Propulsion Directorate Principal Chemical Engineer and Acting Branch Chief on 18 January 2012. Therefore, record is now fully releasable to the public. Attached is a copy of it which has been remarked accordingly.

If you have any questions, please contact me at (937) 522-3091 or DSN 672-3091 or Lynn.kane@wpafb.af.mil.

Sincerely,

A handwritten signature in black ink, appearing to read "L Kane", is positioned above the printed name.

LYNN KANE
Freedom of Information Act Analyst
Base Information Management Section
Knowledge Operations

3 Attachments

1. FOIA Request # 2012-01297-F
2. Copy of AFMC Form 559
3. CD with responsive records, remarked