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**PREPARATION OF HIGH PURITY
ANHYDROUS FERROUS CHLORIDE**

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-1040

March 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7353, Task No. 73530

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(Prepared under Contract No. AF 33(616)-8187
by the Isomet Corporation, Palisades Park, N. J.;
Horace W. Chandler and Joseph Malgiolio, authors.)

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FOREWORD

This report is a detailed summary of all work done on the subject contract. This work was performed at Isomet Corporation, Palisades Park, New Jersey, during the period from March 14, 1961 to September 14, 1962. The work was performed by Dr. Horace W. Chandler and Joseph Malgiolio under Contract No. AF 33 (616)-8187 in support of Project No. 7353, Task No. 735304.

Mr. J.S. Taylor and A2C James J. Nilles, Advanced Metallurgical Studies Branch, Metals and Ceramics Laboratory, Directorate of Materials and Processes, served as contract monitors.

In addition to this report, over 3 kilograms of high purity anhydrous ferrous chloride were delivered to the project sponsor.

Several methods for preparing high purity anhydrous ferrous chloride were investigated. The technique finally developed involved the high temperature chlorination of iron sponge with anhydrous hydrogen chloride and collection of the sublimed ferrous chloride in a condenser held at such a temperature that ferric chloride did not condense.

Ferric iron was undetectable in the final product and other impurities were well below the specified limits. Over 3 kilograms of high purity anhydrous ferrous chloride were prepared by this technique.

This technical documentary report has been reviewed and is approved.

E. M. Kennedy Jr.

E. M. KENNEDY, JR., Lt. Col., USAF
Chief, Advanced Metallurgical Studies Branch
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INTRODUCTION

The preparation of high purity anhydrous ferrous chloride is made difficult by the following factors:

1. Ferrous ion is readily oxidized to ferric ion.
2. The anhydrous salt is deliquescent.
3. Hydrolysis takes place easily in the presence of moisture.

The strong tendency of ferrous ion to oxidize to ferric ion may be attributed to the extreme insolubility of the oxide, which is readily formed by hydrolysis in aqueous solution or in the presence of moisture.

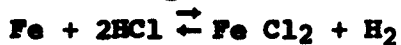
The successful synthesis of hyperpure materials requires, in addition to a satisfactory synthetic route, at least three basic capabilities; rigorously clean preparative facilities, reliable analytical procedures and equipment for determining the purity of the end products, and suitable packaging means and methods.

Ferrous halides have been used to grow iron whiskers (1,2,3). Brenner produced iron whiskers by the thermal decomposition of Fe Cl_2 and Fe Br_2 in a stream of dry, pure hydrogen at $730^\circ\text{--}760^\circ\text{C}$. He was not able to grow whiskers from Fe F_2 . Gorsuch showed that only Fe Cl_2 and Fe Br_2 produced whiskers. Other compounds such as Fe (OH)_2 and mixtures such as $\text{Fe - NH}_4\text{Cl}$ became effective by producing Fe Cl_2 in situ. Most of the whiskers whose properties have been investigated are not exceptionally pure. Iron whiskers grown by Brenner from Fe Br_2 contained 100 ppm. of copper. Contaminants present in the ferrous halides will appear in the whiskers unless they volatilize easily at the reaction temperature.

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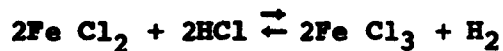
BACKGROUND INFORMATION

An examination of the thermodynamics of ferrous chloride formation is instructive. Figure 1 shows the free energy of formation of ferrous chloride and hydrogen chloride as a function of temperature. It will be noted that at any temperature below about 950°C, the formation of Fe Cl₂ by the reaction



is favored. It therefore appears that anhydrous Fe Cl₂ could be prepared by the treatment of iron with anhydrous HCl at any temperature up to about 950°C.

A possible competing reaction is the following:



Since the free energy of formation of Fe Cl₃ is about -80 kcal./mole, it is seen that the above reaction does not favor the formation of Fe Cl₃. Any Fe Cl₃ that may form is, however, far more volatile than the Fe Cl₂ so that it would not condense at the temperature at which the Fe Cl₂ condenses. It would thus be removed from the reaction and condensation zone and so not contaminate the Fe Cl₂ product.

An alternate technique for preparation of Fe Cl₂ could be the chlorination of iron with dry chlorine. In this case, however, the formation of Fe Cl₃ would be favored and one would obtain a product containing mostly Fe Cl₃.

In addition to the purely anhydrous methods of preparing Fe Cl₂, techniques involving production in aqueous media with subsequent dehydration to the anhydrous salt have been described. In general, these techniques involve the reaction of iron with hydrochloric acid in aqueous solution followed by recrystallization and vacuum drying in the presence of hydrogen chloride. Aqueous techniques, however, require the most rigid precautions to avoid hydrolysis. Because of the existence of several hydrates, the vacuum drying must be carried out under carefully controlled temperature conditions.

The requirements of this program follow. Methods for producing hyperpure anhydrous ferrous halide salts were to be investigated and evaluated with the following considerations:

1. Attainment of a minimum purity of 99.99%
2. All impurities present in amounts greater than 10 ppm. were to be determined for each lot of

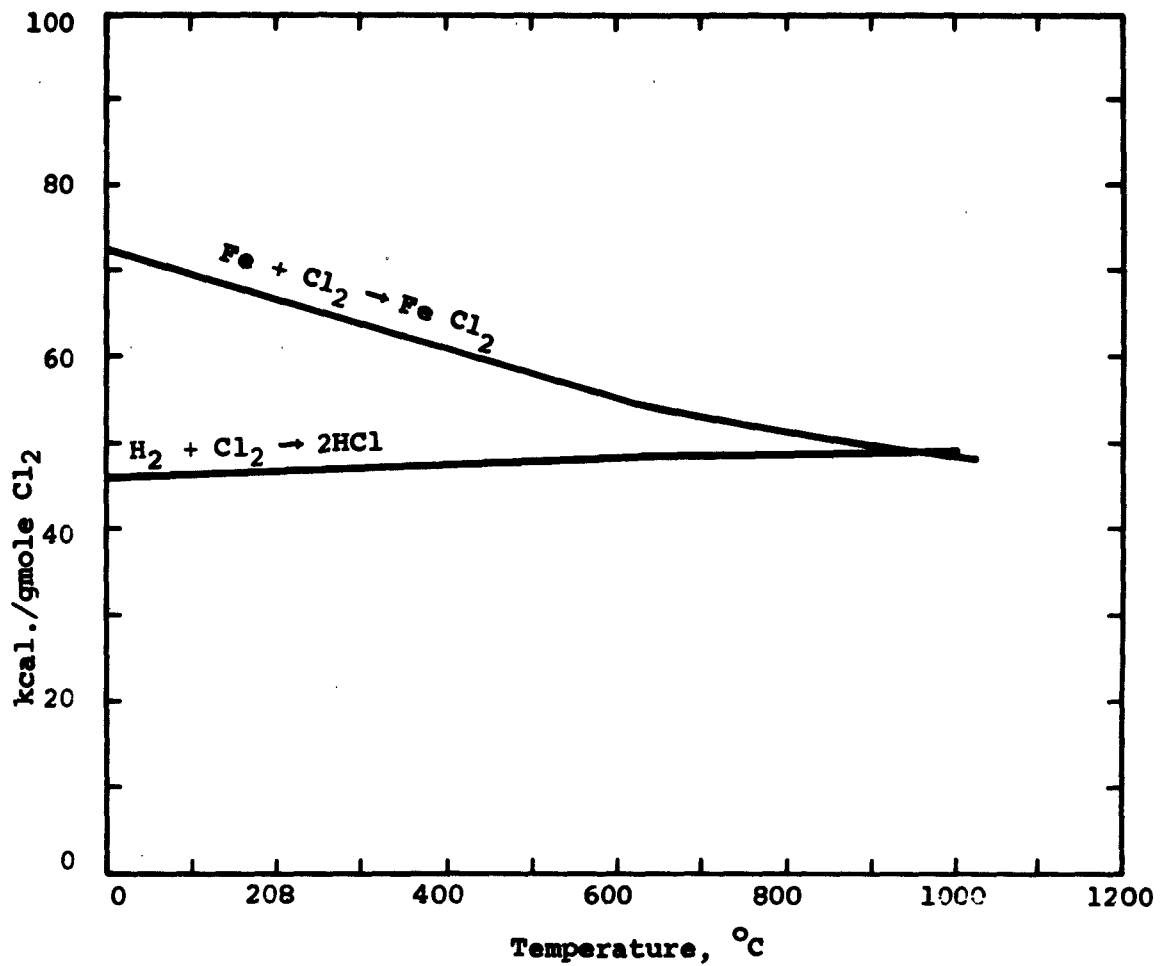


Figure 1. Free Energy of Formation of HCl and FeCl₂ as a Function of Temperature

salt produced. Analyses were to give composition and amount of such impurities.

3. Methods of production should be suitable for quantities of 50-250 grams per two-week period.
4. Packaging techniques shall be developed to avoid contamination and deterioration of the salts during storage and shipment.

The procedure finally developed satisfied these requirements and over 3 kilograms of high-purity anhydrous ferrous chloride produced by this technique were packaged and shipped to the sponsoring agency.

EXPERIMENTAL PROGRAM

High purity, anhydrous, ferrous chloride was prepared by the reaction of high purity iron with anhydrous hydrogen chloride at 900°C. The use of drybox techniques assured anhydrous conditions during the packaging procedure.

A. Materials

Metallic iron, in the form of 200-300 mesh powder was obtained from Johnson, Matthey & Co., Limited, 78-83 Hatton Garden, London, E.C.1, England. This iron is high-purity spectrographically standardised material and is supplied with an individual spectrographic analysis for each batch. The batch of iron used in the preparation of the anhydrous Fe Cl₂ was supplied with the following spectrographic analysis for impurities in parts per million: Si 5, Mn 4, Al, Mg, Ni 2, Cu and Ag less than 1. Sought but not detected were: As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mo, Na, Nb, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

The gases obtained from the Matheson Company were the following:

H₂, electrolytic grade, 99.8% minimum purity
N₂, extra dry grade, 99.7% minimum purity
HCl, anhydrous, 99.0% minimum purity

An independent check on the purity of the iron samples was made by submitting a sample to Lucius Pitkin, Inc. for spectrographic analysis. The following results were obtained:

<u>Element</u>	<u>Concentration, %</u>
Iron	Major
Nickel	0.0X
Silicon	0.00X (low)
Calcium	Not found
Magnesium	Not found
Aluminum	Not found
Copper	0.00X (low)
Molybdenum	0.00X (low)

Elements checked but not found: Zn, Cd, In, Bi, Sb, As, Pb, Sn, Mn, Cr, Co, V, W, Ti, Zr, Th, Ga, Ge, Ag, Ba, Na, Sr, K, Li.

Since the analysis performed by Lucius Pitkin, Inc. did not appear to agree with that supplied by Johnson, Matthey, Inc., particularly with respect to nickel analysis, an independent analysis of a sample was made for nickel using the dimethyl glyoxime technique. This analysis indicated the presence of from

2 to 4 parts per million of nickel, agreeing well with the analysis supplied by Johnson, Matthey Inc. Based on this analysis and the general agreement for other impurities between the Lucius Pitkin and Johnson, Matthey Inc. analyses, it was decided that the iron analyses as provided by Johnson, Matthey Inc. were correct and that the level of impurities was well within the limits specified.

B. Apparatus

The system in which the reaction of iron with hydrogen chloride is carried out is shown in Figure 2. Each of the gases used has a separate entrance line to facilitate gas changes once the reaction procedure has been started. A Drierite column for moisture removal precedes a flow meter and manometer. The gas exits from the reactor through a trapping system. Oxygen is removed from the nitrogen by a copper wire purifier at 400°C.

The reaction is carried out in a vycor tube one inch in diameter by 36 inches long. The tube is crimped 15 inches from one end to about 1/3 of its initial diameter. The barrier formed by the crimp served to divide the reactor into two sections and eliminates contamination of the final product by the iron powder. The 15-inch front section, which constitutes the reaction portion of the tube, is maintained at 900°C during the reaction period, while the portion of the tube on the other side of the crimp is maintained at 400°C and serves as the Fe Cl₂ condenser.

An 8 cubic foot plexiglass drybox equipped with rubber gloves was used to handle the anhydrous Fe Cl₂. The box was modified to allow purging with dry nitrogen. The nitrogen was dried by passage through a 2-inch diameter column, 12 inches long packed with Linde Co. "molecular sieve."

C. Procedure

The iron powder is placed in the center of the 15-inch reaction chamber using a stainless steel spatula. Care is taken during the filling of this section to avoid plugging the reaction tube. Following the filling of the reaction section, oxygen and moisture are removed from the iron and both the reaction and condenser sections by heating the entire vycor tube to 900°C in a flowing hydrogen atmosphere. The condenser section is maintained at 900°C during this process in order to eliminate moisture condensation before the cold traps on the exit end of the reactor. As an added precaution, aluminum foil is wrapped around the entire section of the system between the condenser and the cold trap in order to prevent moisture condensation before the cold trap. After all oxygen and

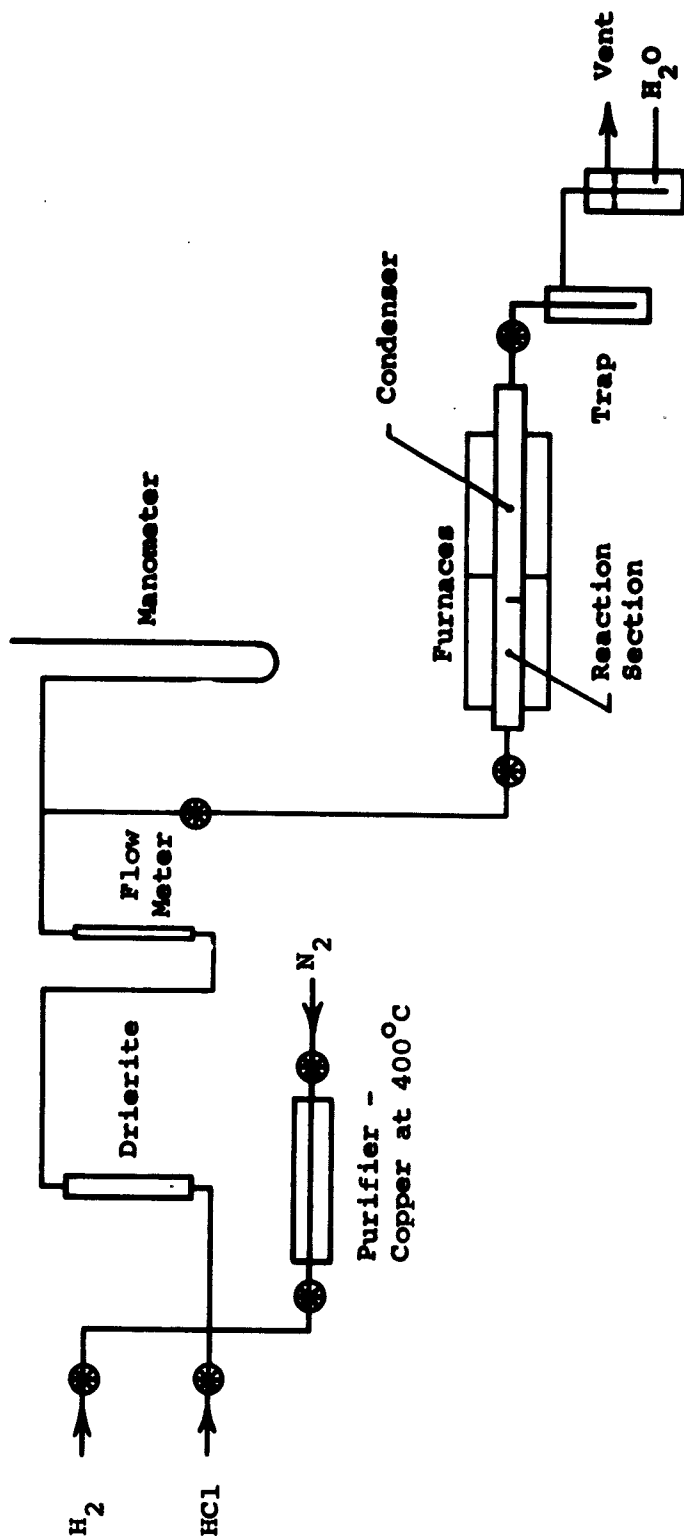


Figure 2. Apparatus for Preparation of Anhydrous FeCl_2

moisture have been removed from the system, the condenser temperature is lowered to 400°C before the hydrogen flow is stopped. At this point, both ends of the vycor tube are closed using the inlet and exit valves, and the moisture-filled cold trap is replaced with a dry one. The vycor tube is then reopened to the rest of the system.

With the reaction section at 900°C and the condenser section at 400°C, anhydrous HCl gas is introduced to the system at a constant feed rate. The initial anhydrous Fe Cl₂ product that sublimes from the 900°C reaction zone to the 400°C condenser appears as crystalline white-yellow particles. As the anhydrous Fe Cl₂ deposit in the condenser becomes more dense, it changes to a red-brown mass. This is particularly true if either molten Fe Cl₂ or melted and refrozen Fe Cl₂ are observed. When all of the iron has reacted, as determined by direct observation of the reaction zone, the temperature in this portion of the vycor tube is lowered to 400°C followed by cooling of both portions of the vycor tube to room temperature.

The residual HCl in the system is removed by purging with nitrogen which has been deoxygenated by passage through hot copper filings and dried by passage through the Drierite. The vycor tube is sealed by closing the inlet and exit valves, disconnected from the remainder of the system, and transferred to the dry box.

When the vycor tube is in the dry box, the box is purged with approximately three volumes of dry nitrogen. Further drying of gas within the dry box is accomplished by placing two open beakers of P₂O₅ in the dry box. The vycor tube is then opened and the Fe Cl₂ is unloaded and lightly ground in an agate mortar with an agate pestle. A one-gram sample of the ground product is retained as a control and the remainder is loaded into approximately 10 amber bottles containing about 15 grams each. Amber bottles are used in order to prevent any degradation of the Fe Cl₂ by sunlight.

The bottles are tightly capped, removed from the dry box and finally sealed by wrapping plastic electrical tape around the cap and bottle and dipping the taped cap into molten paraffin.

Over 3 kilograms of high purity, anhydrous Fe Cl₂ were prepared, packaged and shipped in this manner.

D. Analysis

Since impurities present in the iron used were shown to be well below the specified limits, the only impurity that

was routinely tested for in the final product was ferric ion. As a precaution and a check on the possible presence of impurities in the final product, an analysis of several samples of Fe Cl_2 for the presence of nickel was carried out since nickel appeared to be the one detectable impurity about which some question existed. These analyses using the colorimetric dimethyl glyoxime technique indicated that nickel was present in the final product to the extent of less than 2 parts per million.

1. Ferric Analysis

Ferric iron reacts with thiocyanate to form an intense red complex, whereas ferrous iron does not. A visual colorimetric comparison is therefore possible for the detection of Fe Cl_3 in Fe Cl_2 . A standard iron solution containing 0.02 grams Fe^{+3} per 100 cc of water was prepared. The thiocyanate reagent was prepared by mixing 100 ml. of 1.5 M KCNS with 40 ml. of 1-to-1 HCl. A standard solution representing the presence of 2×10^{-5} grams of Fe^{+3} is prepared by adding 0.1 ml. of the standard Fe^{+3} solution to 10 ml. of distilled water and 1 ml. of the acidic KCNS solution. One gram of the anhydrous Fe Cl_2 is dissolved in 10 ml. of distilled water and 1 ml. of the standard KCNS solution is added. The unknown and the standard are compared. The limit of detection of Fe Cl_3 present in Fe Cl_2 is 20 parts per million because of the yellow-green color caused by the presence of the large amount of Fe Cl_2 in the solution. In all samples the Fe^{+3} was present below this level since no red color was detected.

2. Nickel Analysis

Nickel is determined spectrophotometrically as the dimethyl glyoxime complex. A sample of either iron or Fe Cl_2 is dissolved in 5-10 ml. of distilled water with 20 ml. of concentrated HNO_3 . The solution is heated to dissolve the sample and then carefully evaporated to dryness. To the residue is added 15 ml. of distilled water and 25 ml. of concentrated HCl to form Fe Cl_3 . This solution is then extracted several times with 25 ml. portions of diethyl ether until the aqueous layer is colorless. About 5 extractions are required when a 2-gram sample is dissolved. The ether layers containing the Fe Cl_3 are discarded.

The aqueous layer is then neutralized with ammonium hydroxide and 10 ml. of ammonium citrate buffer solution (pH=9-9.5) are added. The final pH of the solution should be 9-9.5. The addition of the citrate buffer serves to adjust the pH and also to complex any traces of Fe^{+3} remaining.

Approximately 50 mg. of hydroxylamine hydrochloride are added to insure the presence of the nickel in the proper oxidation state. The nickel is complexed by adding 5 ml. of 1% dimethyl glyoxime solution in ethanol and waiting 5-10 minutes for

the complex to form. The complex is extracted into 5 ml. of chloroform and the transmission of the chloroform solution is measured at 375 m μ . The amount of nickel present is estimated using an extinction coefficient calculated from the transmission of known amounts of nickel dimethyl glyoxime in chloroform.

CONCLUSIONS

High purity, anhydrous Fe Cl₂ can be prepared by treatment of high purity Johnson, Matthey Inc., iron powder with anhydrous HCl at 900°C and collecting the sublimed product at 400°C. The product is packaged using drybox techniques. The product contains no detectable impurities above the levels specified.

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APPENDIX

Aqueous methods for preparing high purity, anhydrous Fe Cl_2 were also investigated in the course of these studies. In general these methods were not found to be as suitable as the anhydrous techniques because of the ever present danger of hydrolysis and the cumbersome nature of the process. The apparatus and technique which appeared to give the most satisfactory results of all the aqueous procedures tried are described here.

A sketch of the apparatus is shown in Figure 3. It consists of a vycor reaction tube (A) with two arms. One of the arms is attached by means of a short rubber connector to both an acid reservoir (B) and a supply of powdered iron (C). The rate of admission of iron into the reactor is controlled by the movement of a hollow glass rod having a ground, tapered end that fits tightly into the ground female bottom of the tube holding the iron powder. The hollow glass rod has a hole in its side through which nitrogen can be admitted. The nitrogen can then flow through this hollow flow-control rod down into the reactor and out the other arm, thereby keeping the system purged of all impurities. The exit arm has a small water-cooled condenser attached to it which serves to condense any vapors carried from the reactor by the flowing nitrogen stream. The acid is stored in a bulb from which it flows by gravity through a control stopcock into the reaction tube. A water bath is placed under the reaction tube to provide for either heating or cooling of the reaction tube.

The hydrochloric acid (36-38% aqueous solution) is placed in the acid storage bulb and dry nitrogen is bubbled through the acid to remove any oxygen. Nitrogen is purified by passage over hot copper filings. Some of the HCl is admitted to the reaction tube. High purity Johnson-Matthey iron powder is added to the iron supply container and the system is then completely purged with the purified nitrogen. The iron is then admitted to the acid at a rate sufficiently slow so as not to cause foaming. Nitrogen is allowed to flow continuously through the system. The rate of admission of the iron is controlled by manipulation of the tapered glass rod. When all of the iron is in the reaction tube, the remainder of the HCl is admitted to the reaction tube, thereby washing any iron powder off the walls of the admission tube. The amount of acid added is very slightly greater than the stoichiometric requirement so as to maintain a reasonable reaction rate.

The water bath is warmed so as to keep the reaction going at a gentle rate without causing excessive foaming from hydrogen evolution. The reaction is continued until all iron is dissolved. At this point the solution is cooled to room temperature. The mother liquor is decanted from the $\text{Fe Cl}_2 \cdot 4\text{H}_2\text{O}$ crystals that form. Decantation is achieved by tilting the apparatus to

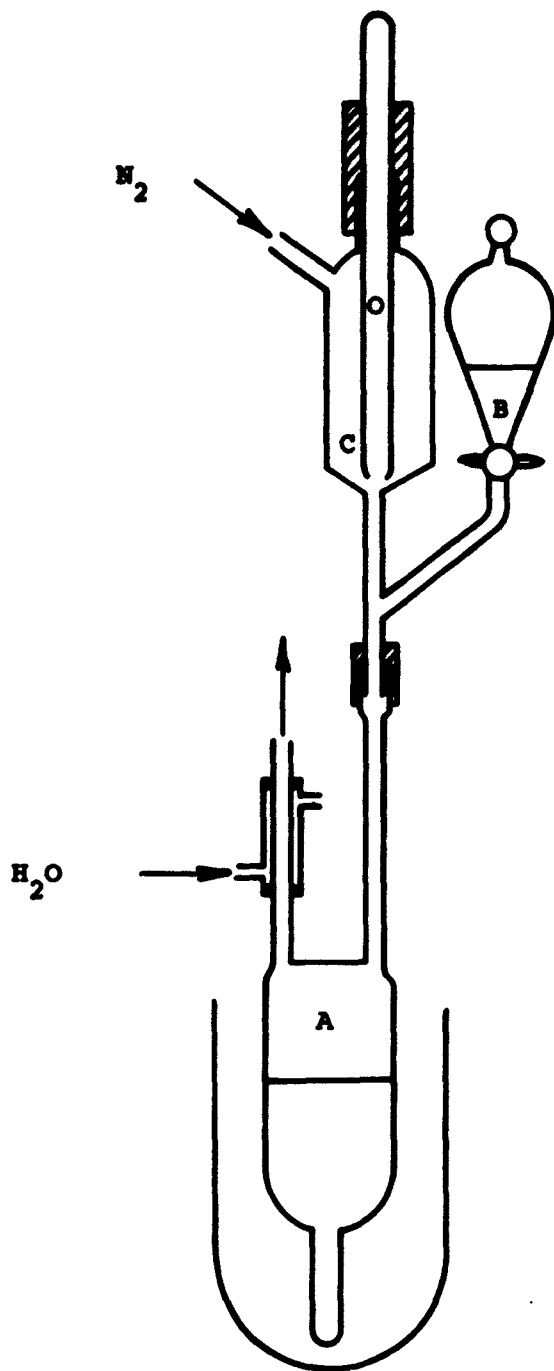


Figure 3. Apparatus for Aqueous Preparation of Anhydrous Fe Cl_2

allow the liquor to flow in the direction of the nitrogen flow.

Various hydrates can form depending upon the temperature. The range of stability of the various hydrates is as follows:

Fe Cl ₂ .6H ₂ O	stable below 12.3°C
Fe Cl ₂ .4H ₂ O	stable from 12.3°C to 72.6°C
Fe Cl ₂ .2H ₂ O	stable from 72.6°C to 120°C
Fe Cl ₂ .H ₂ O	forms from Fe Cl ₂ .2H ₂ O above 120°C

Removal of the final water of hydration occurs at 150°-200°C under reduced pressure. In view of these temperature ranges, the dehydration is carried out by slow heating in a stream of nitrogen and HCl gas to prevent hydrolysis. After all visible water is removed the final product is heated to 250°C under high vacuum to ensure complete dehydration. In order to test for complete dehydration, a tube containing P₂O₅ mixed with bromcresol purple is inserted in the exit line from the reactor. Any moisture in the vapor above the product will form phosphoric acid with the P₂O₅ and cause a color change in the bromcresol purple indicator.

- I. Iron compounds and chlorides
- I. AFSC Project 7353, Task 735304
- II. Contract AF 33(616)-8187
- III. Isomet Corp. Palisades Park, N.J.
- IV. H. W. Chandler, Joseph Malgiolio
- V. Aval fr OTS
- VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals & Ceramics Lab, Wright-Patterson AFB, Ohio.
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