

STUDIES ON THE FERRIC CHLORIDE-GRAPHITE SYSTEM

by

MICHAEL WILLIAM BARTLETT

B.Sc. (Hons), University of British Columbia, 1965

A THESIS PRESENTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

May, 1967

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date May 19, 1967

ABSTRACT:

Isotherms of the ferric chloride-graphite system have been determined at 300°C, 310°C, and 350°C. It was found that C_7FeCl_3 is formed at all three temperatures, and in addition $C_{12}FeCl_3$ is formed at 350°C.

C_7FeCl_3 has been isolated by preparing it in a bomb. Mössbauer studies on it showed that electron transfer is from graphite to iron chloride, and that all of the iron is in the same oxidation state.

It has been shown that intercalated ferric chloride can be reduced to ferrous chloride by hydrogen at 375°C.

Studies on graphite containing ferric chloride or chromyl chloride have shown that the threshold pressure for intercalation of Br_2 , ICl , or CrO_2Cl_2 is higher than for pure graphite.

It has been found that the uptake of chromyl chloride by graphite is dependent on the rate of pressure increase, and that in addition natural crystals of graphite vary in their reactivity with chromyl chloride.

TABLE OF CONTENTS:

Introduction	1
Experimental	5
Results	13
Discussion	24
Bibliography	38

LIST OF TABLES:

TABLE I

Page 37

LIST OF FIGURES:

- (1) High Temperature Vacuum Recording Thermobalance
- (2) Isotherm of ferric chloride on SP-1 at 300°C
- (3) Isotherm of ferric chloride on SP-1 at 350°C
- (4) Isotherm of ferric chloride on PG-1 at 300°C
- (5) Isotherm of iodine monochloride on $C_{64}CrO_2Cl_2$ at 20°C
- (6) Isotherm of iodine monochloride on $C_{100}CrO_2Cl_2$ at 20°C
- (7) Isotherm of bromine on $C_{64}CrO_2Cl_2$ at 20°C
- (8) Isotherm of bromine on $C_{100}CrO_2Cl_2$ at 20°C
- (9) Isotherm of iodine monochloride on C_7FeCl_3 at 20°C
- (10) Isotherm of bromine on C_7FeCl_3 at 20°C
- (11) Mössbauer Spectra of $FeCl_3$, C_7FeCl_3 , and of Reduced C_7FeCl_3

ACKNOWLEDGEMENT:

I would like to express my gratitude to Dr. J. G. Hooley who so ably directed this research.

I would also like to thank Dr. J. R. Sams, Dr. B. V. Liengme, and Mr. J. C. Scott for running the Mössbauer spectrometer used in this study and for many helpful discussions on the spectra obtained and their interpretation.

I would also like to thank Dr. F. Einstein for his aid in obtaining X-ray powder photographs.

INTRODUCTION:

The purpose of this work was to determine composition versus pressure isotherms of the ferric chloride-graphite system. The value of such a study can best be appreciated by examining some of the results obtained from isotherms of similar systems.

Early results for the bromine-graphite system gave varying compositions for graphite-bromide. The compositions C_8Br , $C_{10}Br$, and $C_{13}Br$ had been reported for the composition stable at saturation (1) (2) (3). Determination of the complete isotherm by Hooley (4) for several kinds of graphite and at different temperatures showed that the compound formed is C_8Br with crystalline natural graphite and that earlier variations were probably due to capillary condensation on different size ranges of graphite. In addition he showed that C_8Br is stable on desorption from 1.0 to 0.5 partial pressure relative to saturation, contradicting an earlier claim that C_8Br is stable only at saturation (5). Another result was that bromine will react with graphite only above a threshold pressure which is 0.05 relative to saturation (for natural graphite). Interpretation of the variation in threshold pressures for a series of pyrolytic graphites of varying degrees of interlayer bonding led to proposal of a mechanism for bromination of graphite (6).

The determination of the isotherm of the ICl -graphite system (4) at $20^\circ C$ showed that two compounds are formed: $C_{16}ICl$ and C_8ICl .

An earlier report (7) had stated that the composition was $C_{5.4}ICl$ at saturation--a result which by examination of the isotherm can be seen to be probably due to capillary condensation. The existence of two compounds of ICl and graphite and their stoichiometry thus became apparent only with an isotherm of the system.

The reaction of CrO_2Cl_2 with graphite was variously reported to yield $C_{17}CrO_2Cl_2$ (8), $C_{12}CrO_2Cl_2$ or $C_{130}CrO_2Cl_2$ (7), depending on reaction conditions. Determination of the isotherm (4) of the system at $20^\circ C$ showed that the compound formed in vapor is $C_{32}CrO_2Cl_2$. In addition, it was shown that the compound thus formed did not desorb provided reaction lasted a day or more. The isotherm also showed that the threshold pressure for intercalation of CrO_2Cl_2 is 0.25 relative to saturation, compared to 0.05 and 0.03 for bromine and iodine monochloride respectively.

This brief account illustrates the value of determining isotherms for reactant-graphite systems. Isotherms demonstrated the existence and stoichiometry of graphite compounds and showed their pressure stability ranges. In addition, interpretation of such features as threshold pressures aided understanding of the mechanism of reaction (6). Hence, it appeared likely that isotherms of the graphite-ferric chloride system would prove of similar value.

Ferric chloride was first shown to react with graphite by Thiele (9). A detailed study by Rüdorff and Schultz (10) claimed that two compounds are formed: $C_{12}FeCl_3$ between $180^\circ C$ and $309^\circ C$ and $C_{30}FeCl_3$ between $325^\circ C$ and $400^\circ C$, both after acid washing of the preparation.

Croft (11) later stated that $C_{30}FeCl_3$ is a decomposition product of the more concentrated compound. In a detailed X-ray and electron-diffraction study of graphite-ferric chloride preparations, Cowley and Ibers (12) showed that $C_{12}FeCl_3$ consists of 17% free graphite. They also showed that more dilute preparations contain more free graphite, and less $FeCl_3$ per layer. Furthermore, they found that if $C_{12}FeCl_3$ is heated to $300^{\circ}C$, free graphite disappeared.

All of these workers prepared graphite-ferric chloride by heating graphite with anhydrous ferric chloride in a bomb for 24 hours at temperatures from $180^{\circ}C$ to $350^{\circ}C$ followed by rapid chilling and washing with HCl to remove unreacted ferric chloride. They thus lacked assurance that their preparations were not decomposition products of equilibrium compositions. It therefore appeared that determination of the isotherm for the graphite-ferric chloride system would improve our understanding of the system.

A second aspect of the graphite-ferric chloride system is the question of the state of ferric chloride in the layers. Hennig made (13) electrical measurements on graphite-ferric chloride. He postulated that ferric chloride is partially ionic and proposed the formula $C_n^+ \cdot FeCl_3^- \cdot 3FeCl_3$. To date, however, there has been no direct evidence for the existence of two oxidation states of iron required by the above formula. It thus appeared that a study of graphite-ferric chloride using Mössbauer spectroscopy might provide either an independent confirmation of the above formula or an alternative to it.

A third topic studied is the form of the isotherm of bromine, iodine monochloride and chromyl chloride on a graphite which initially has in it the saturation amount of chromyl or ferric chloride. Some previous work (14) showed that $C_{32}CrO_2Cl_2$ for instance would not intercalate bromine even at saturation. The threshold pressure for ICl was higher than for graphite and the ICl uptake at higher pressures was only half that of pure graphite. These interesting observations were extended by using chromyl chloride residues of various compositions and by similarly examining graphite containing ferric chloride.

Finally, an interesting observation that slowly raising chromyl chloride pressure from zero to saturation prevents measureable intercalation of chromyl chloride by graphite (15) formed the basis for some further studies. These studies were based on the detection of reaction by expansion of the graphite normal to the layer planes.

EXPERIMENTAL:

A. CHEMICALS:

- (a) Bromine: Reagent grade material was distilled into the balance reservoir, the middle fraction being retained.
- (b) Iodine monochloride: British Drug House reagent grade material was distilled into the balance reservoir, with the fraction coming over at 101°C and 760 mm pressure being retained.
- (c) Chromyl chloride: The CrO_2Cl_2 was supplied by the Allied Chemical and Dye Company of New York. The fraction distilling at 116°C and 760 mm pressure was retained.

The above three reagents were stored in subdued light. They were deaerated until they contained less than 3×10^{-5} cm Hg air pressure.

- (d) Anhydrous Ferric Chloride: Anhydrous ferric chloride was prepared by direct reaction of iron (99.85% Fe, Baker and Adamson Standardization Grade) with chlorine gas dried by passage through concentrated sulphuric acid and over phosphorus pentoxide. The resulting product was sublimed in the presence of chlorine into vials provided with break-seals. After the vials were filled with ferric chloride, the chlorine was condensed into a liquid nitrogen trap and the vials were pumped with a mercury diffusion pump to less than 10^{-4} cm Hg. The vials were then sealed off under vacuum.
- (e) Graphite: several types were used.
 - (i) National Spectroscopic Grade SP-1. Supplied by the National Carbon Company, Cleveland, Ohio.

This is a highly purified natural graphite and was used without further purification. Flake size was 0.02 to 0.1 mm across.

- (ii) Madagascar graphite. This had been previously purified by alternate extractions from HF and HCl. The size range employed was 60-70 mesh.
- (iii) New York graphite. Acid extracted from marble deposits in Essex county, New York. Individual crystals were hand picked under a microscope after extraction, and had been treated with alternate extractions with HF and HCl. The flake size employed was about 3 mm diameter (parallel to the layer planes) and 0.1 to 0.7 mm thick.
- (iv) Pyrolytic graphite. Polynucleated at 2150°C, density 2.21 gm/cm³, and supplied by High Temperature Laboratories, Boston, Mass. The sample employed in this study consisted of 10 discs of diameter 2.6 mm and 1.0 mm thickness. This graphite was designated PG-1 in an earlier study (6) and will be so designated in this work.

B. EQUIPMENT:

The isotherms with bromine, Iodine monochloride, and chromyl chloride were studied in a recording vacuum thermobalance equipped with a recording spoon gage. (16) (17). The sensitivities employed were about 6 mv/mg or 1 mv/mg for weight and 60 mv/cm for pressure.

Before admission of a reactant, the system was pumped with a mercury diffusion pump to less than 10^{-4} mm (as measured with a McLeod gage), and it was verified that it would hold this vacuum overnight. Taps in contact with the reactant vapors were greased with Kel-F; all other taps and joints were greased with Apiezon-N. Pressure was reduced by opening the system to a trap cooled in liquid nitrogen. The reactor tube was held at 20° by a thermostatted bath.

Expansion studies were made in an apparatus which held graphite samples with their layer planes normal to the viewing axis of a microscope fitted with a micrometer eyepiece (6). Magnifications employed were x37.5 or x75, depending on the sample size. Except when the samples were actually being viewed, the sample tube was surrounded with a thermostatted jacketed at 20° .

Isotherms with ferric chloride were made in a modified version of the recording thermobalance, (16) diagrammed in figure 1. All parts of the apparatus containing FeCl_3 were heated by resistance furnaces. The pressure of FeCl_3 was controlled by varying the temperature of the FeCl_3 reservoir, and was measured by the pyrex spiral gauge.

The FeCl_3 reservoir, the pyrex spring, and the sample were each thermostatted to within 0.5°C by "Proportionull 1300 Series" temperature controllers, supplied by Cole-Parmer Instrument and Equipment Company. The sensing elements were Platinum resistors. The furnaces were constructed with two windings: the bulk of the heating was supplied by heavy windings, while a second and lighter winding supplied control heating.

The linear variable differential transformer was a high temperature model (#060XS-FT), supplied by Schaevitz Engineering, Ltd, of N. Jersey. It was suspended from two iron rings mounted near the top of the balance tube. The second iron ring was supported on the first by three brass screws, "A", and had three more screws, "B", which passed through holes in the second ring. (See detail drawing of figure 1). Silica fibres suspended from these screws "B" were hooked onto a glass support ring attached to the LVDT. The screws the fibres hung on served to allow for slight differences in the fibre lengths. The other three screws "A" allowed for moving the whole LVDT up or down relative to the core. They were fitted with special heads so that a screwdriver could be used to adjust the LVDT when the furnace was hot. The silica spring was the same type employed in the room temperature thermobalance (16). The sensitivity of the balance was about 1 mv/mg in the range 300°C - 350°C . All temperatures were measured with Leeds and Northrup duplex iron-constantan thermocouples, stated to be within 1/3% of the temperature reading in Centigrade degrees as determined from NBS

calibration tables. An ice bath was used to cool the reference junctions.

Samples were introduced into the balance by lowering the spring, LVDT core, sample bucket and connecting silica fibres into the balance tube. The connecting tube and FeCl_3 reservoir (complete with an unopened FeCl_3 vial) were then blown onto the top of the balance tube and connected to the vacuum system. The system was pumped to less than 10^{-4} cm using a mercury diffusion pump. The FeCl_3 vial's breakseal was then broken with a magnetic hammer. The system was sealed off under vacuum at the point indicated on the diagram (figure 1). The balance tube was then brought up to the temperature selected for the isotherm (300°C , 310°C , or 350°C in this work), leaving the ferric chloride unheated. As soon as thermal equilibrium was reached, the LVDT was adjusted to give a suitable output, and the lamp for illuminating the spiral gage's mirror was adjusted. The ferric chloride reservoir was then heated to give a desired vapor pressure. The pressure was measured by admitting air to the envelope of the spiral gage to return the reflected spot of light from the gage to a null point, and then measuring the air pressure with a mercury manometer. At the conclusion of a run, air was re-admitted by carefully cracking the balance tube and admitting air to the envelope at the same rate.

The spring--LVDT combination was calibrated by replacing the pyrex spiral gage section of the balance tube with a support tube. A long silica fibre hung from the core and passed through the bottom of the furnace into a plastic box.

The box served to keep drafts from affecting weight readings. The balance was then calibrated by adding known weights to a small glass pan hung from the silica fibre. The temperature of the spring and LVDT were kept as close as possible to the temperatures they would be at during isotherms. It was found that the sensitivity of the balance decreased with increasing temperature, so calibrations were made for the actual temperatures used. Silica springs are known to contract on increasing temperature, so the spring was kept at a constant temperature during a run.

Buoyancy due to ferric chloride vapor was compensated for by corrections derived from a blank run with the balance completely assembled, but without a sample. The decrease in the apparent weight of the sample bucket with increasing ferric chloride vapor pressure was observed and assumed to be due to buoyancy.

Several preparations of graphite-ferric chloride were also made in bombs. Some of the bomb preparations were carried out in stainless steel #304 bombs which were loaded with a weighed sample of graphite plus anhydrous ferric chloride in a dry box with an oxygen-free nitrogen atmosphere. The sealed bomb was then heated to 300°C for 24 hours, after which it was opened and the product washed free of excess ferric chloride by washing on a fritted glass funnel with 6N HCl until the washings gave no red colour with KSCN solution. This method was found to give irreproducible results when more than 100 mg of graphite was employed. Accordingly, a modified technique was employed: an inverted U-shaped glass reactor was sealed

to a vacuum line; one arm contained a weighed sample of graphite, the other a 10% excess of iron wire necessary to form C_7FeCl_3 (previously shown to be the most concentrated compound formed between graphite and ferric chloride). The apparatus was then evacuated to less than 1 micron pressure, and a stream of chlorine dried by passage through concentrated sulphuric acid and over phosphorus pentoxide was passed through the apparatus. The iron wire was gently heated with a torch until reaction started. After all the iron had reacted with chlorine, the chlorine was condensed into a trap cooled in liquid nitrogen, and the apparatus was pumped to less than 10^{-4} cm with a mercury diffusion pump and sealed off. It was then heated as described above, or, in several runs, with separate temperature controls for the graphite and ferric chloride arms.

Two attempts to reduce intercalated ferric chloride in C_7FeCl_3 to ferrous chloride were carried out with samples placed in a zirconia boat within a silica tube heated to $375^{\circ}C$ in a stream of hydrogen (22). The hydrogen had been purified by passage through concentrated sulphuric acid and over copper turnings at $500^{\circ}C$, followed by passage over phosphorus pentoxide.

X-ray powder photographs of several of the graphite-ferric chloride preparations were taken for identification purposes only. Cu Ka radiation at 35 kV and 15 mA using 0.5 mm capillaries were used for all photographs. Exposure times were 8-15 hr.

Mössbauer spectra of several of the graphite-ferric chloride preparations were obtained from the laboratories of Dr. J. R. Sams. The gamma ray source was ^{57}Co in a copper matrix. All of the data are shown in table I. All figures are in mm/sec relative to N. B. S. standard sodium nitroprusside ($\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$), N. B. S. standard material #725.

RESULTS:

FERRIC CHLORIDE ISOTHERMS ON GRAPHITE

The isotherm of ferric chloride on SP-1 at 300°C from zero pressure to saturation is shown in figure 2. At each pressure, it was found that about 24 hours were required to reach a weight constant to $\pm 1\%$. Note that the threshold pressure was below the pressure gage's sensitivity which was 0.25 cm Hg, that C_7FeCl_3 is the only pressure independent composition observed, and that the final residue had a mole ratio ($C/FeCl_3$) of 25. Before the balance was opened, the isotherm was repeated. The threshold pressure was again below the sensitivity of the gage, the absorption curve led smoothly into the previous one, and the desorption curve was duplicated. Finally, a fresh sample of SP-1 gave exactly the same isotherm as shown in figure 2.

Since an earlier report (10) had indicated that only $C_{30}FeCl_3$ is formed above 309°C, an isotherm at 310°C was run on SP-1. The resulting isotherm was similar to figure 2 with the features stretched along the pressure axis. The threshold pressure for intercalation was measureable this time and was about 0.75 cm Hg. The only pressure independent composition was C_7FeCl_3 , as before, and the mole ratio of the residue ($C/FeCl_3$) was 33--somewhat higher.

It was decided to investigate details of the low pressure part of the isotherm by running an isotherm at 350°C (figure 3). The isotherm runs from zero pressure to one atmosphere, rather than to saturation which is 7 atmospheres at this temperature (18). This limitation was imposed by the inability of the

glass system to hold 7 atmospheres pressure. The threshold pressure is about 1.5 cm Hg, and $C_{12}FeCl_3$ in the range 20-40 cm Hg (0.04-0.08 relative to saturation). Above the latter pressure C_7FeCl_3 is formed. Note that the failure to observe $C_{12}FeCl_3$ in the 300°C and 310°C isotherms may have resulted from the narrow relative pressure range in which it is stable--this range would be about 1 cm Hg at 300°C. On desorption $C_{10}FeCl_3$ is a pressure independent composition in the range 12-8cm Hg. This decomposes to a residue whose mole ratio of C to $FeCl_3$ is 50. A second run was made on this residue before opening the balance and confirmed the $C_{12}FeCl_3$ plateau.

From the absorption curves at 300°C, 310°C, and 350°C Arrhenius plots at compositions 0.020, 0.040, and 0.060 ($FeCl_3/C$) were made. The three slopes gave an isosteric heat of 13.0 ± 1.0 kcal/mole with no trend with composition.

It was decided to investigate the influence of using a less perfect graphite than SP-1 on the isotherm (6). The isotherm of $FeCl_3$ on a PG-1 sample at 300°C is shown in figure 4 (for a description of this sample and its dimensions, see "Experimental"). Note that the threshold pressure is about 15 cm Hg, and that the pressure independent composition is about $C_{12}FeCl_3$ which decomposes to a residue compound of mole ratio (C/ $FeCl_3$) 31 at about 0.5 cm Hg. The sample had split into thin discs during the run. It is of interest to note that PG-1 also splits into thin discs during reaction with bromine (6). The apparent increase in weight on desorption will be discussed later.

A significant feature of all these runs was that the pressure in the system fell to zero when the temperature was finally reduced to 20°C at the end of a run. There is hence no Cl_2 left in the gas phase and therefore the iron in the graphite is there as FeCl_3 or $2\text{FeCl}_2 + \text{Cl}_2$. There was also no evidence for the production of an FeCl_2 residue in the balance system. This means that the iron is in the graphite as FeCl_3 and not ~~X~~ as a mixture of FeCl_3 and Cl_2 .

BOMB PREPARATIONS OF GRAPHITE-FERRIC CHLORIDE

In order to study some properties of the compounds observed during the isotherms, it was decided to attempt their preparation in bombs which could be rapidly chilled to room temperature.

A stainless steel #304 bomb was loaded with 0.1 gm SP-1 and 1 gm FeCl_3 in a dry nitrogen atmosphere. After 24 hours at 300°C, it was chilled rapidly in cold water, opened and washed free of excess FeCl_3 with 6M HCl. In a second run, the bomb was cooled at 10°C per hour for 24 hours (after having been heated at 300°C for 24 hours). Both products were $\text{C}_{12}\text{FeCl}_3$ which is the approximate composition reported by previous workers (10) (11) (28). Apparently, these two rates of cooling gave the same amounts of kinetic trapping in the central region of the graphite crystals (14) (19). The Mössbauer spectra of these 2 preparations will be described later (table I).

Attempts to prepare more $\text{C}_{12}\text{FeCl}_3$ in the same bomb using 500 mg SP-1 and 1500 mg FeCl_3 gave preparations of compositions $\text{C}_{20-30}\text{FeCl}_3$. It was concluded that the 3 cm of graphite in the

bomb bucket was so deep that ferric chloride was not able to diffuse through the nitrogen to the bottom and react in the 24 hours exposure.

As described in "Experimental" all of the preparations in stainless steel bombs were loaded in dry oxygen-free nitrogen atmosphere. The possibility that the resulting two atmospheres pressure of nitrogen (at about 600°K) would slow diffusion of ferric chloride into the finely powdered SP-1 was eliminated by using evacuated glass bombs with the ferric chloride prepared in situ. Glass bombs also had the possible advantage of cooling more rapidly than the thick stainless steel bombs; rapid cooling should remove the metal chloride from the peripheral areas of the graphite crystals and allow the graphite to drop to its normal interlayer distance, thus preventing more ferric chloride from diffusing out and giving a higher composition (14) (19). A third possible advantage was the elimination of metallic iron which could reduce FeCl_3 to FeCl_2 . A run to check this last possibility showed that a piece of stainless steel #304 of the same surface area as the bombs does react with ferric chloride vapor. The stainless steel, after 24 hours exposure to ferric chloride at 300°C, was coated with brown ferrous chloride.

Several preparations in glass bombs with air cooling did give C_7FeCl_3 after acid washing. This product had a Mössbauer spectrum similar to that of anhydrous ferric chloride (33) (34) in that it consisted of a single peak. This peak was shifted from 0.69 mm/sec of FeCl_3 (at room temperature) to 0.77 mm/sec (also at room temperature).

The 002 and 004 lines of graphite were absent from the X-ray powder photograph of this C_7FeCl_3 . Asher and Wilson (32) have stated if as little as 5% free graphite were present then these intense lines would show in the powder photograph. In addition the powder photograph of this C_7FeCl_3 had no lines coincident with those of anhydrous ferric chloride.

An attempt to remove more $FeCl_3$ from C_7FeCl_3 by extracting with 6M HCl in a Soxhlet for 24 hours removed less than 1 mg from 700 mg of compound. This result could be explained by suggesting that the acid is prevented from reaching the ferric chloride by a skin of graphite around the edges of the crystals. If so, then slower cooling of a bomb might allow more ferric chloride to diffuse out during cooling. Accordingly, a glass bomb, after heating for 24 hours at $300^{\circ}C$, was cooled at $10^{\circ}C/hour$ for 24 hours. The product, however, was again C_7FeCl_3 , even after 4 hours washing with boiling 6M HCl. Slower rates were not used.

It was decided to attempt preparation of the $C_{12}FeCl_3$ observed during the $350^{\circ}C$ isotherm. This was prepared in an inverted U-tube reactor. One arm, containing the SP-1, was maintained at $350^{\circ}C$; the other, containing ferric chloride, was maintained at $295^{\circ}C$ (at which temperature the vapor pressure of ferric chloride is 30 cm Hg, the middle of the $C_{12}FeCl_3$ plateau observed in the isotherm). After 24 hours the tube was cooled in air, opened and acid extracted with 6M HCl until the washings gave no red colouration with KSCN. The product was $C_{12}FeCl_3$.

Two attempts were made to prepare $C_{12}FeCl_3$ by subliming $FeCl_3$ off C_7FeCl_3 and then acid washing (10). The inverted U-tube reactor described above was used. After heating the graphite at $300^\circ C$ and the ferric chloride at $295^\circ C$ for 24 hours (a combination known (see figure 2) from the isotherm to give C_7FeCl_3) the arm not containing graphite was chilled in an air blast until no more $FeCl_3$ could be seen condensing. Thus, pressure was reduced rapidly without chilling the sample. After this, the other arm was cooled to room temperature over a period of 15 minutes. According to Rüdorff (10) this procedure should yield an acid-washed product of $C_{12}FeCl_3$. The product, however, was C_7FeCl_3 after acid washing.

C_7FeCl_3 was reduced at $375^\circ C$ in oxygen-free hydrogen in two different runs (22). The X-ray powder photograph of the product in each case was similar but not identical to that of C_7FeCl_3 : several of the lines were shifted slightly, and the intensity ratios of the lines had changed. There was no evidence of either free graphite (no graphite 002 or 004 lines) or of free ferric chloride. The Mössbauer spectrum was very different from that of C_7FeCl_3 , and resembled that of ferrous chloride (24).

ISOTHERMS OF BROMINE, IODINE MONOCHLORIDE, AND CHROMYL CHLORIDE ON GRAPHITE-CHROMYL CHLORIDE AND GRAPHITE-FERRIC CHLORIDE RESIDUES

Ferric chloride and chromyl chloride are unique in that their amounts in graphite at saturation can be retained on reducing the pressure to zero. The effect of this retention on the absorption properties of graphite was the subject of this study. Bromine, iodine monochloride, and chromyl chloride

were used for the comparison because they cover a range of threshold pressures and mole ratios of their compounds with graphite.

A. CHROMYL CHLORIDE RESIDUES

The maximum uptake of CrO_2Cl_2 by graphite from the vapor at 20°C is $\text{C}_{32}\text{CrO}_2\text{Cl}_2$ (4). Residue compounds containing one-half ($\text{C}_{64}\text{CrO}_2\text{Cl}_2$) and one-third ($\text{C}_{100}\text{CrO}_2\text{Cl}_2$) were prepared by reacting 60-70 mesh Madagascar graphite in chromyl chloride vapor for 48 hours at a pressure known to give these ratios as equilibrium compositions. Madagascar graphite was used because it is easy to obtain large samples of uniform flake size and high purity of this graphite. Large samples were used so that any variation in reactivity from flake to flake would be averaged out.

It was found that neither of the chromyl chloride residue compounds would intercalate more CrO_2Cl_2 when the vapor was admitted in several steps to saturation. One run with $\text{C}_{64}\text{CrO}_2\text{Cl}_2$ in which chromyl chloride vapor was admitted directly to saturation, and then lowered just below that pressure gave an uptake bringing the total to $\text{C}_{45}\text{CrO}_2\text{Cl}_2$, still below the equilibrium value of $\text{C}_{32}\text{CrO}_2\text{Cl}_2$ for unreacted graphite.

ICl reacted with both chromyl chloride preparations. The isotherms are shown in figure 5 and figure 6. A threshold pressure of 0.1 cm Hg was observed for both. One pressure-independent composition was observed on desorption for each residue. The mole ratios were (C/ICl) 16 for $\text{C}_{100}\text{CrO}_2\text{Cl}_2$ and 25 for $\text{C}_{64}\text{CrO}_2\text{Cl}_2$.

Bromine also reacted with both chromyl chloride residues. The threshold pressure for intercalation was 2.0 cm Hg for both residues. Again, one pressure-independent composition was observed on desorption for each residue. The mole ratios were (C/Br) 12 in $C_{100}CrO_2Cl_2$ and 16 in $C_{64}CrO_2Cl_2$. Note that no bromine is taken up by $C_{32}CrO_2Cl_2$ (4). Fig 7
Fig 8

It was decided to attempt preparation of a more concentrated chromyl chloride-graphite compound, $C_{16}CrO_2Cl_2$, according to Croft's method (8). The purpose of preparing this more concentrated compound was to find the threshold pressure for intercalation of ICl in it. Three attempts using vacuum distilled chromyl chloride at 100°C in a glass bomb with the reaction carried out in darkness for 24 hours resulted in formation of only $C_{40}CrO_2Cl_2$. This suggests that Croft's product may have contained some hydrolysis products of CrO_2Cl_2 rather than CrO_2Cl_2 alone.

B. FERRIC CHLORIDE RESIDUES

C_7FeCl_3 prepared in a glass bomb from SP-1 formed the basis for a similar set of runs to test its reactivity. It was found that CrO_2Cl_2 does not react with C_7FeCl_3 . ICl reacts, but the resulting isotherm is very different from that for the pure graphite. The isotherm is shown in figure 9. The threshold pressure for intercalation is 0.15 cm Hg, higher than for the original graphite (4). There is no evidence for the formation of $C_{16}ICl$ or C_8ICl on absorption or desorption. $C_{10}ICl$ forms on desorption. A residue $C_{40}ICl$ is left after reduction of pressure to zero, which is about the same as the residue left by ICl on pure graphite (4).

Bromine also reacts with C_7FeCl_3 . The isotherm is shown in figure 10. Note the initial weight decrease as bromine was added. Assuming the threshold pressure to be where the weight first increased above its original value, then it is about 9 cm Hg. There is no pressure-independent composition. The residue has a mole ratio (C/Br) of about 50, roughly the same as in pure graphite (4). A second run on this residue failed to show significant uptake.

STUDIES OF THE REACTION OF CrO_2Cl_2 WITH GRAPHITE

Several studies of the expansion of New York graphite in CrO_2Cl_2 vapor were made with the purpose of investigating the observation that slowly raising chromyl chloride vapor to saturation prevents measureable intercalation (15). Hooley and Garby (15) found that if chromyl chloride is admitted slowly (spending about 2 days with the chromyl chloride pressure below the normal threshold pressure of 0.4 cm Hg (4), there is no expansion normal to the layer planes. They also showed that the action of the chromyl chloride must be on the peripheral regions of the crystals, for if the New York graphite crystals previously treated in chromyl chloride vapor are edge-trimmed and then exposed to saturated CrO_2Cl_2 vapor they expanded immediately. The possibility that surface absorbed water reacted with chromyl chloride to form an impermeable layer was eliminated in this study by heating several New York graphite crystals to $1100^{\circ}C$ while pumping with a mercury diffusion pump: chromyl chloride vapor was then admitted at the above rate. There was again no expansion.

Attempts to duplicate these observations were only partially successful. Although it was always found that raising the pressure slowly prevented any measureable expansion, edge trimming did not restore every crystal's ability to expand when exposed to saturated CrO_2Cl_2 vapor. As these measurements were made at the limit of the optical system's sensitivity, it was decided to construct a more sensitive device to measure expansion before continuing. A recording expansion meter is now being developed, and has been employed in some preliminary studies (21) on the bromination of graphite.

The above variation in the behavior of New York crystals in chromyl chloride vapor promoted a study to check on an earlier claim (22) that New York graphite crystals thicker than 0.4 mm (normal to the layer planes) do not expand when exposed to saturated chromyl chloride vapor. It was found that if chromyl chloride is admitted in one step to saturation, even New York crystals as thick as 0.75 mm normal to the layer planes would expand to about 150% of their original length. It was found that exposing a crystal so expanded (and held in CrO_2Cl_2 vapor for 24 hours) to bromine at 14.5 cm Hg caused no further expansion. Exposure of a crystal previously expanded in chromyl chloride to ICl vapor at 0.3 cm Hg caused no further expansion; raising the ICl pressure to 1.9 cm Hg caused the crystal to expand a further 20% of its original length. These results are in qualitative agreement with the results of Hooley (4) on isotherms of bromine and iodine monochloride on $\text{C}_{32}\text{CrO}_2\text{Cl}_2$ referred to in the Introduction.

This finding that thick crystals will expand when exposed immediately to saturated chromyl chloride vapor prompted a final study to determine whether chromyl chloride intercalation begins in the end planes of natural graphite crystals. The method used was that of Hooley, Garby, and Valentin (6). A thick New York crystal had two markings of ZnO and Dow Corning "Silastic" adhesive painted on its side, splitting the length normal to the layer planes into three nearly equal divisions. On exposure to saturated chromyl chloride vapor, all three sections began expanding at the same time, but at different rates. This result may still be consistent with intercalation beginning in the end planes, provided there are variations in interlayer bonding within single crystals of New York graphite (6).

It does appear that New York graphite crystals do vary in their behavior in chromyl chloride perhaps ^{because} of varying amounts of interlayer bonding or other imperfections. It also appears that there is a slow reaction over a period of about 24 hours in graphite-chromyl chloride which prevents or at least decreases further intercalation.

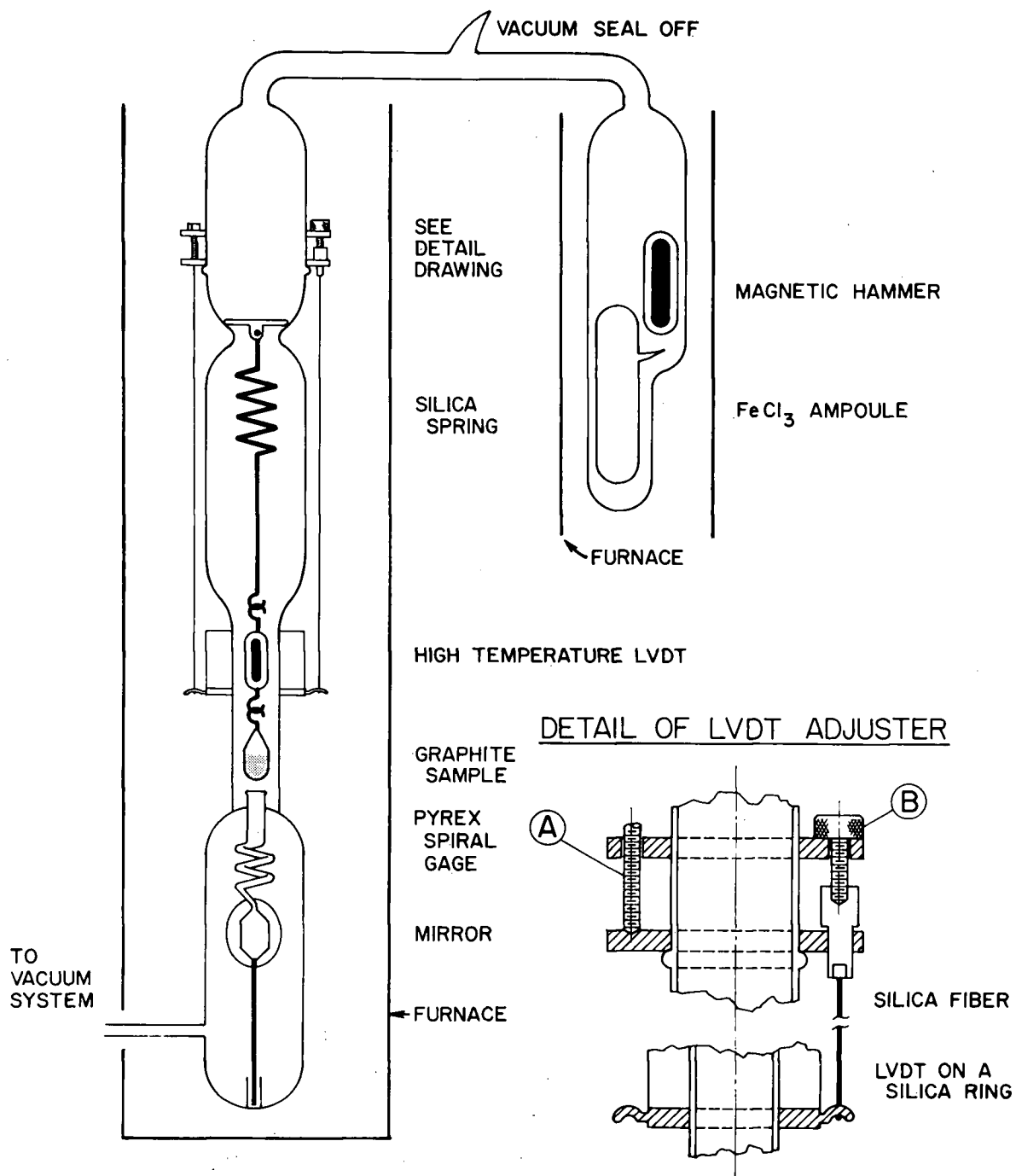
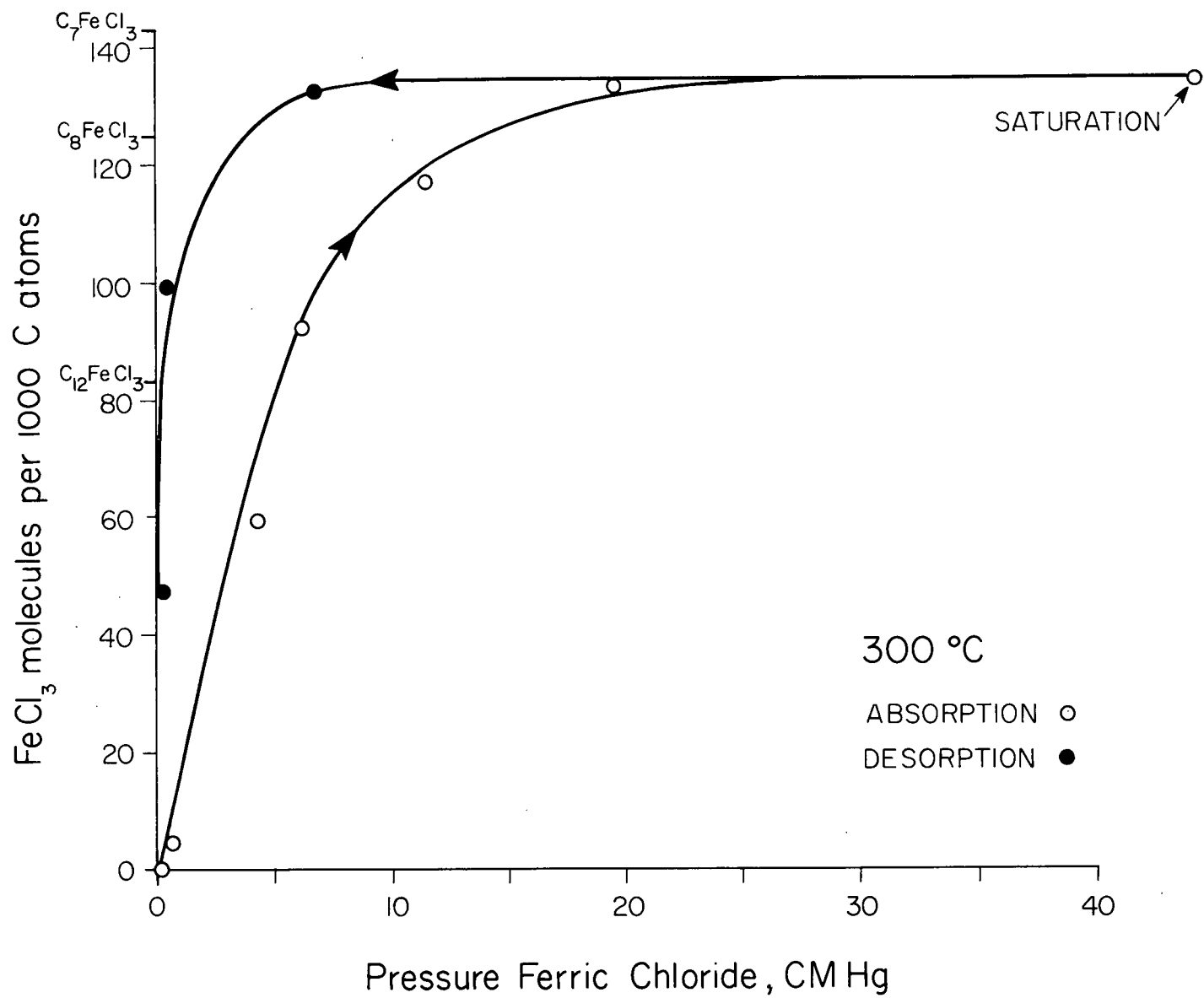


Figure 1: High Temperature Vacuum Recording Thermobalance

Figure 2: Isotherm of ferric chloride on SP-1 at 300°C



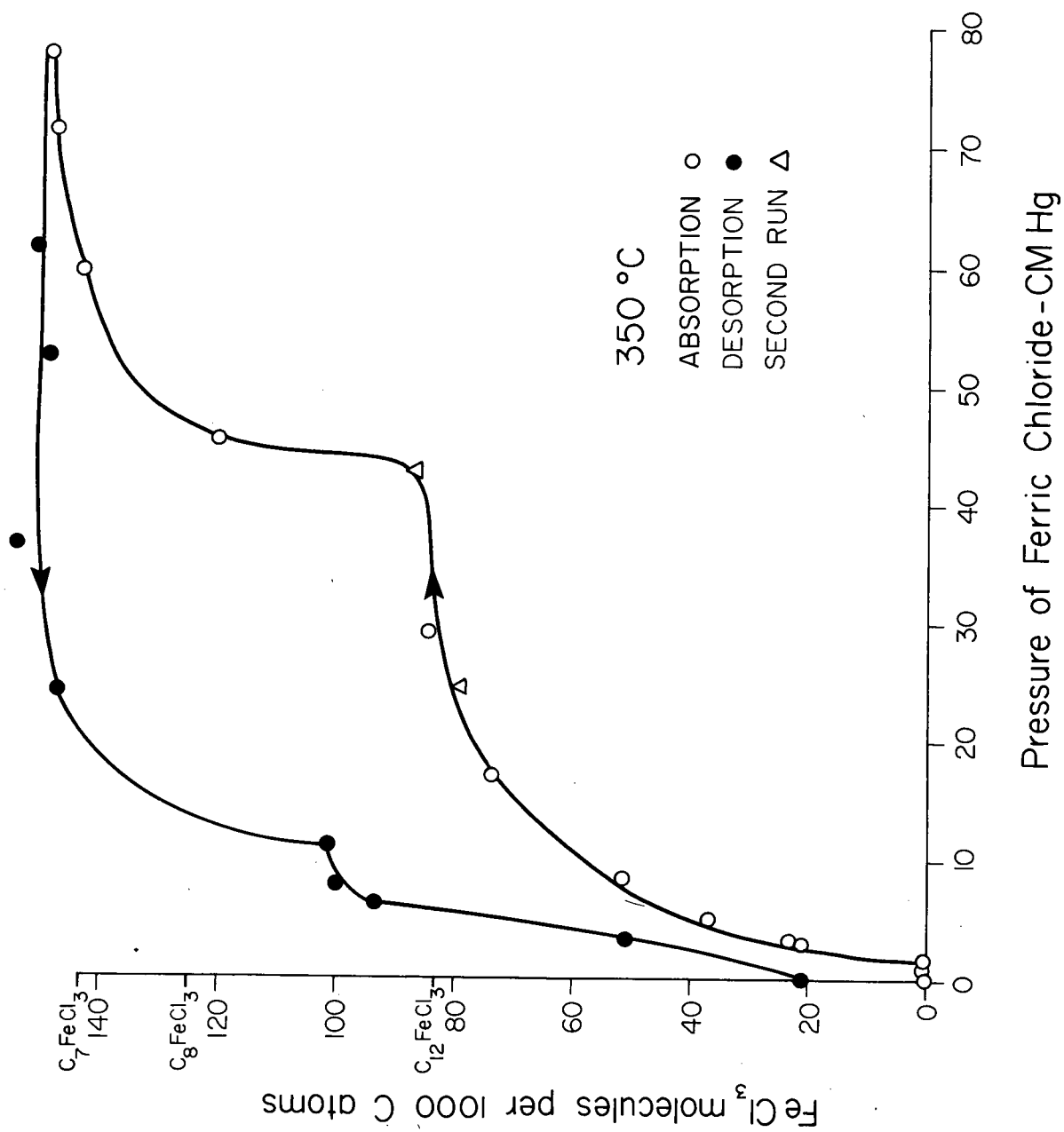


Figure 3: Isotherm of ferric chloride on SP-1 at 350°C

Figure 4: Isotherm of ferric chloride on PG-1 at 300°C

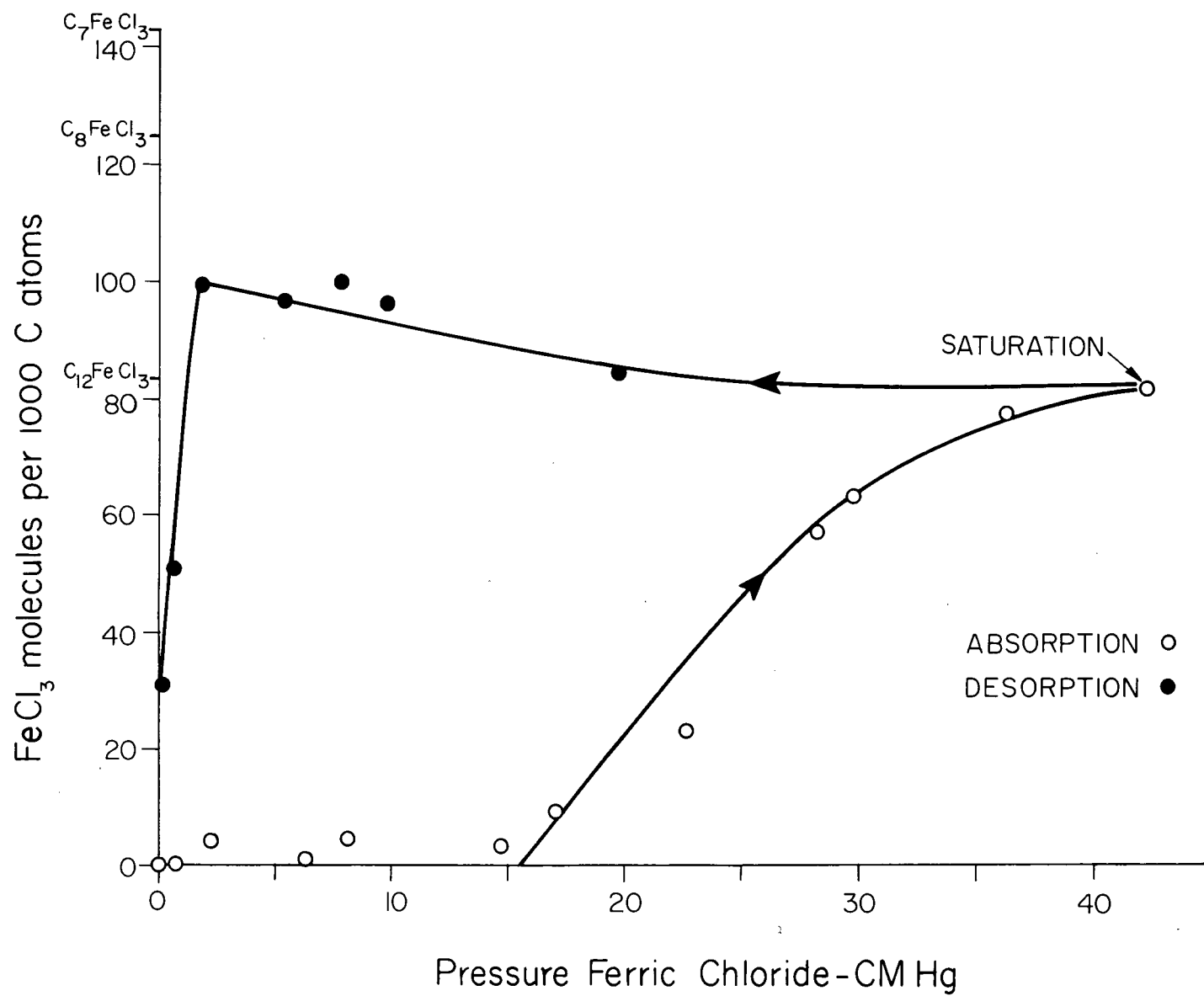


Figure 5: Isotherm of iodine monochloride on $C_{64}CrO_2Cl_2$ at $20^\circ C$

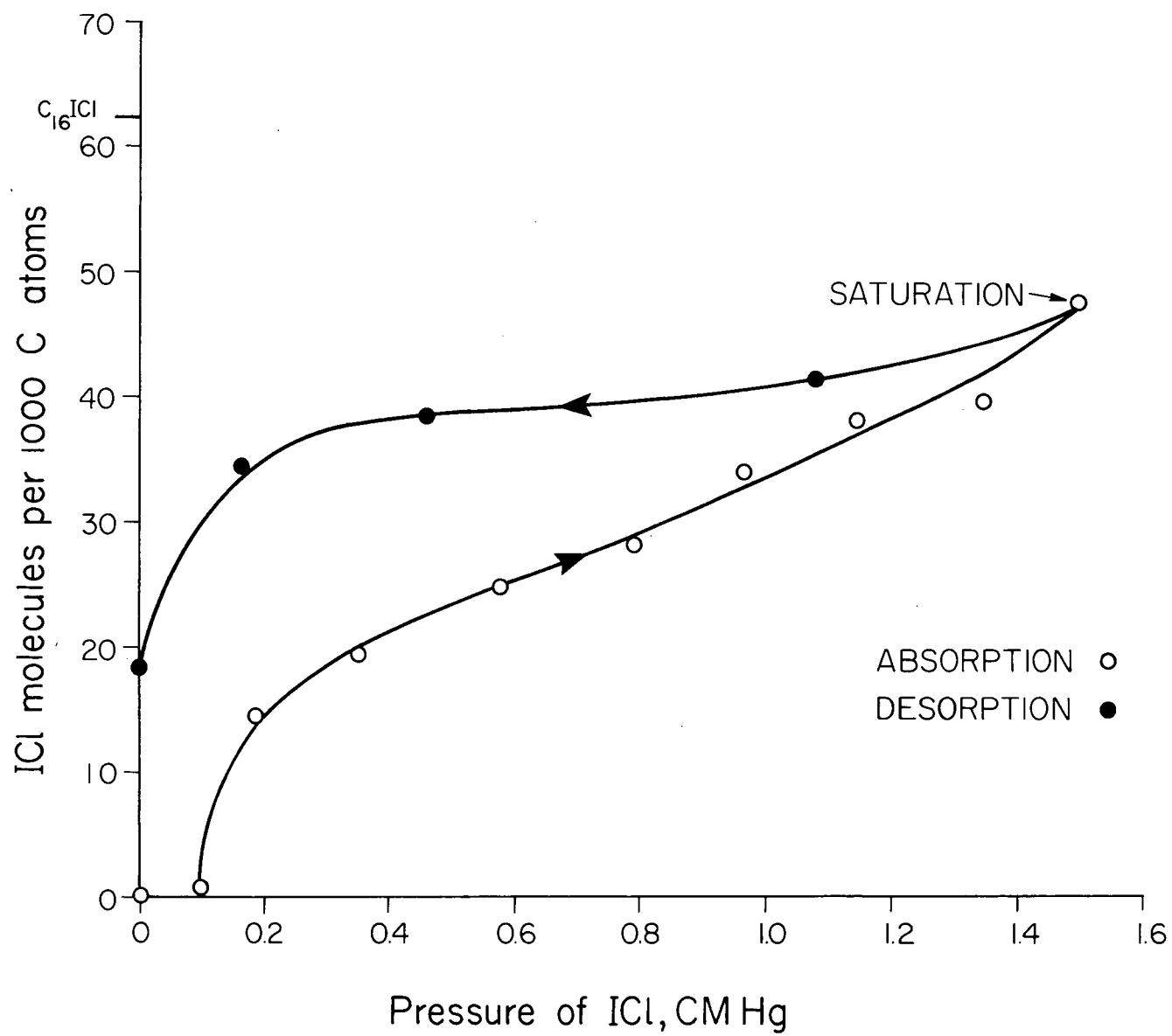


Figure 6: Isotherm of iodine monochloride on $C_{100}CrO_2Cl_2$ at $20^\circ C$

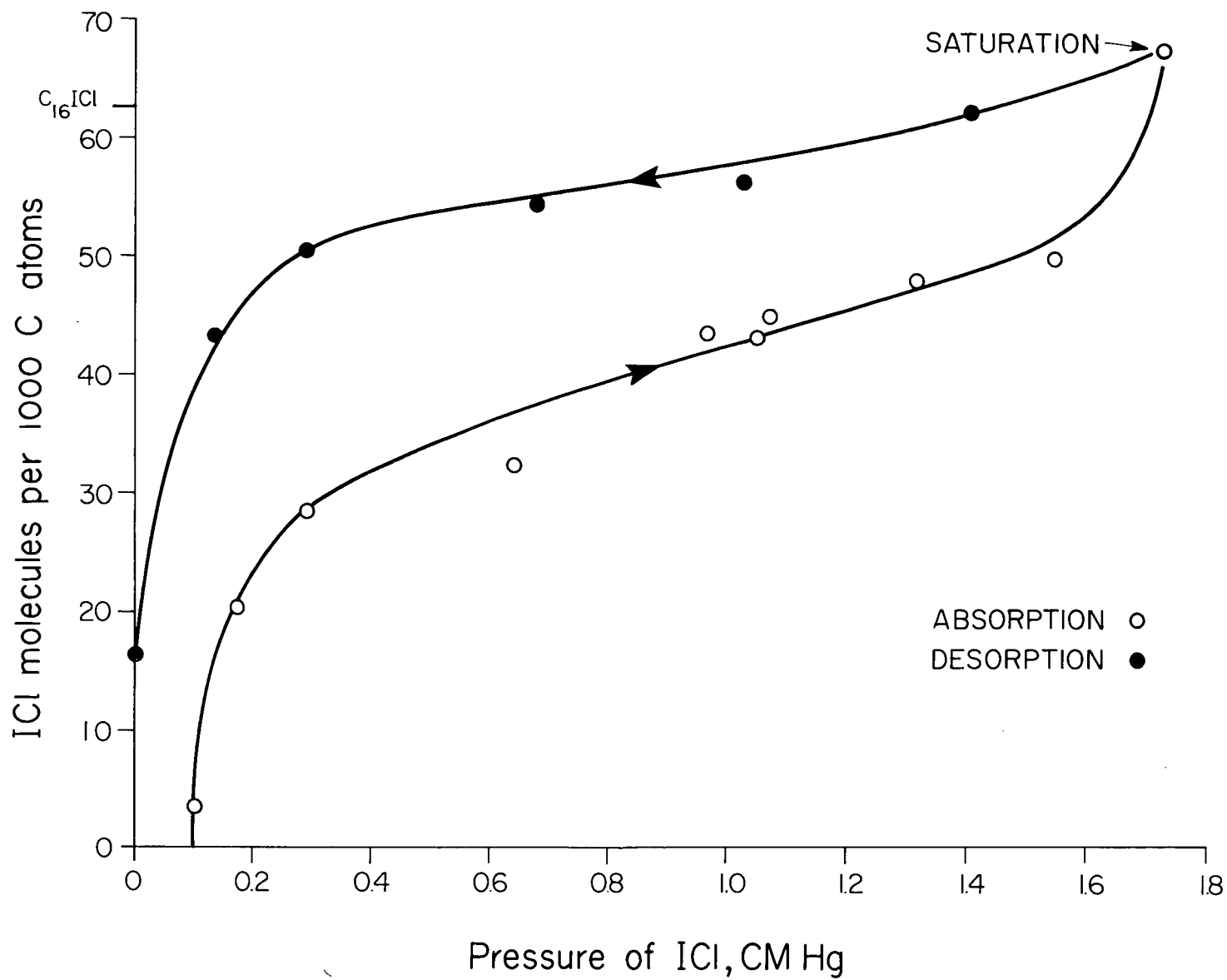
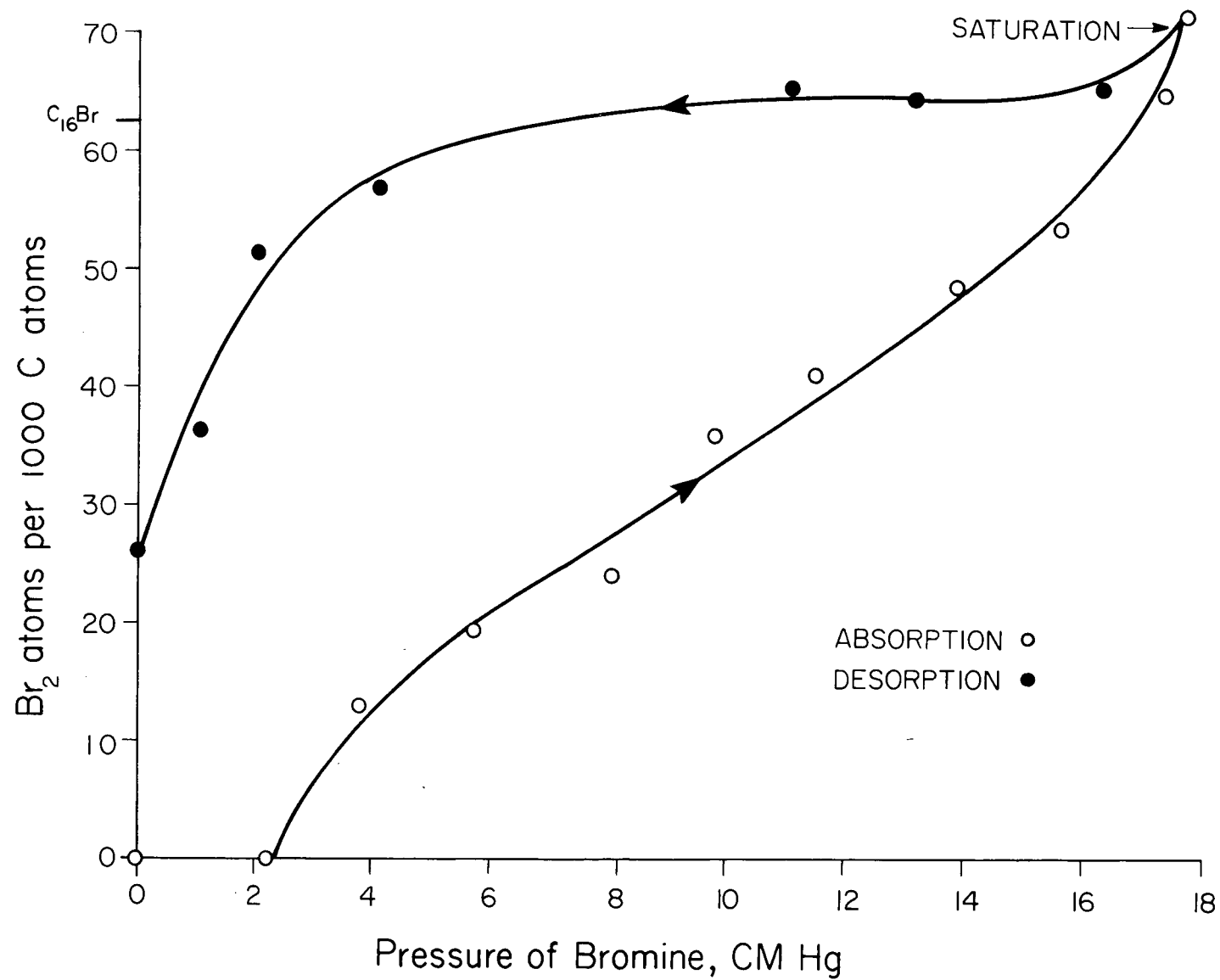


Figure 7: Isotherm of bromine on $C_{64}CrO_2Cl_2$ at $20^\circ C$



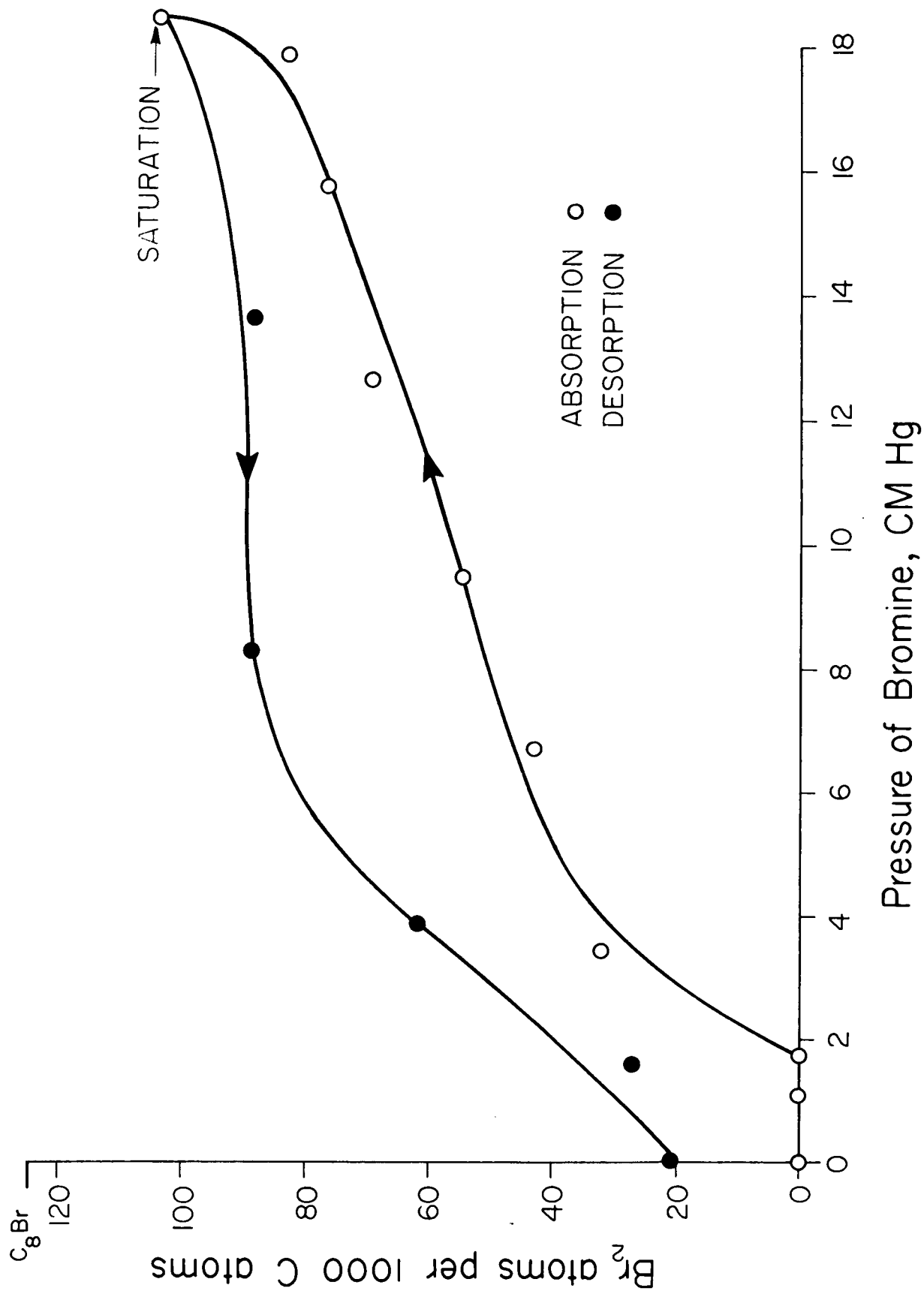
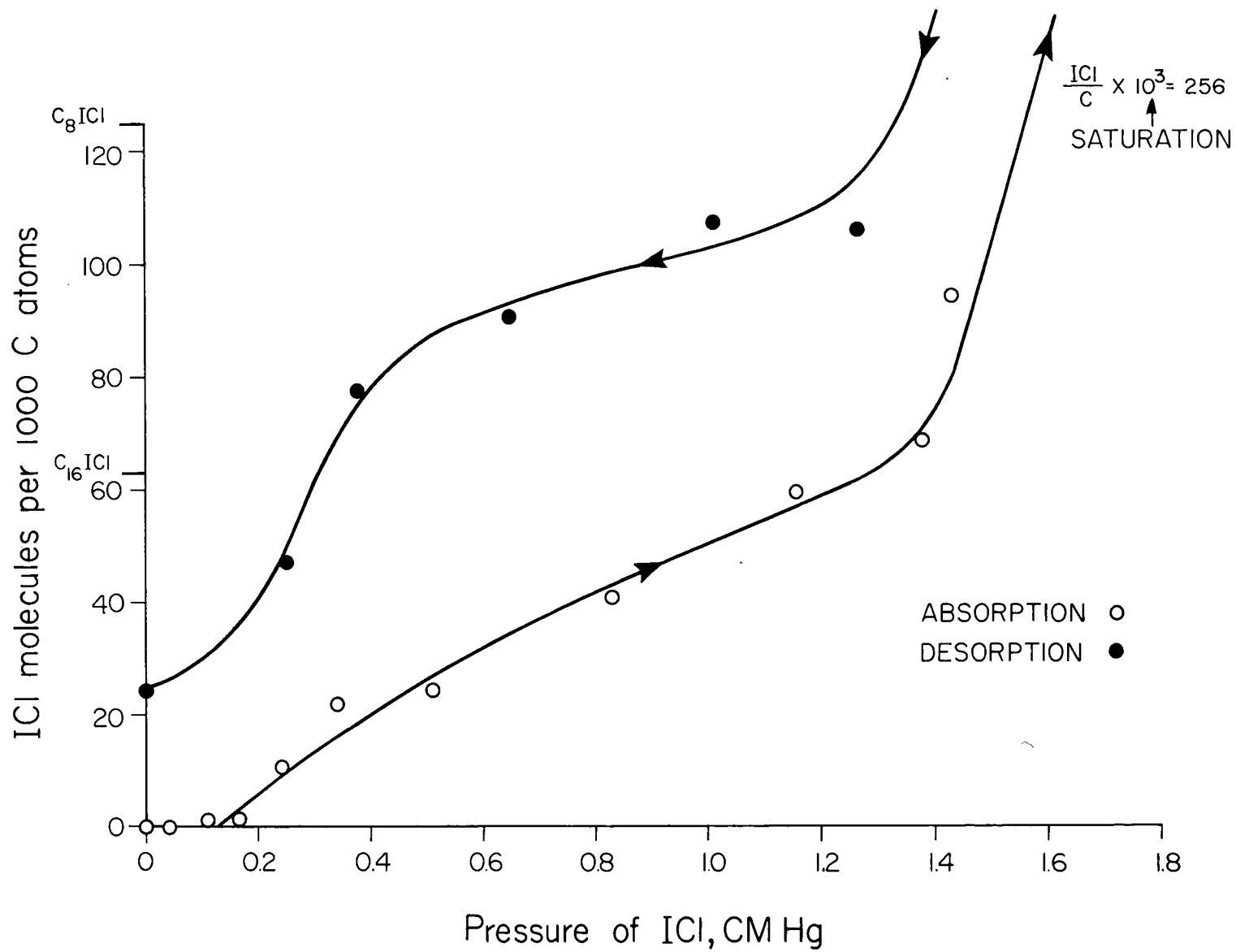


Figure 8: Isotherm of bromine on $\text{C}_{100}\text{CrO}_2\text{Cl}_2$ at 20°C

Figure 9: Isotherm of iodine monochloride on C_7FeCl_3 at $20^\circ C$



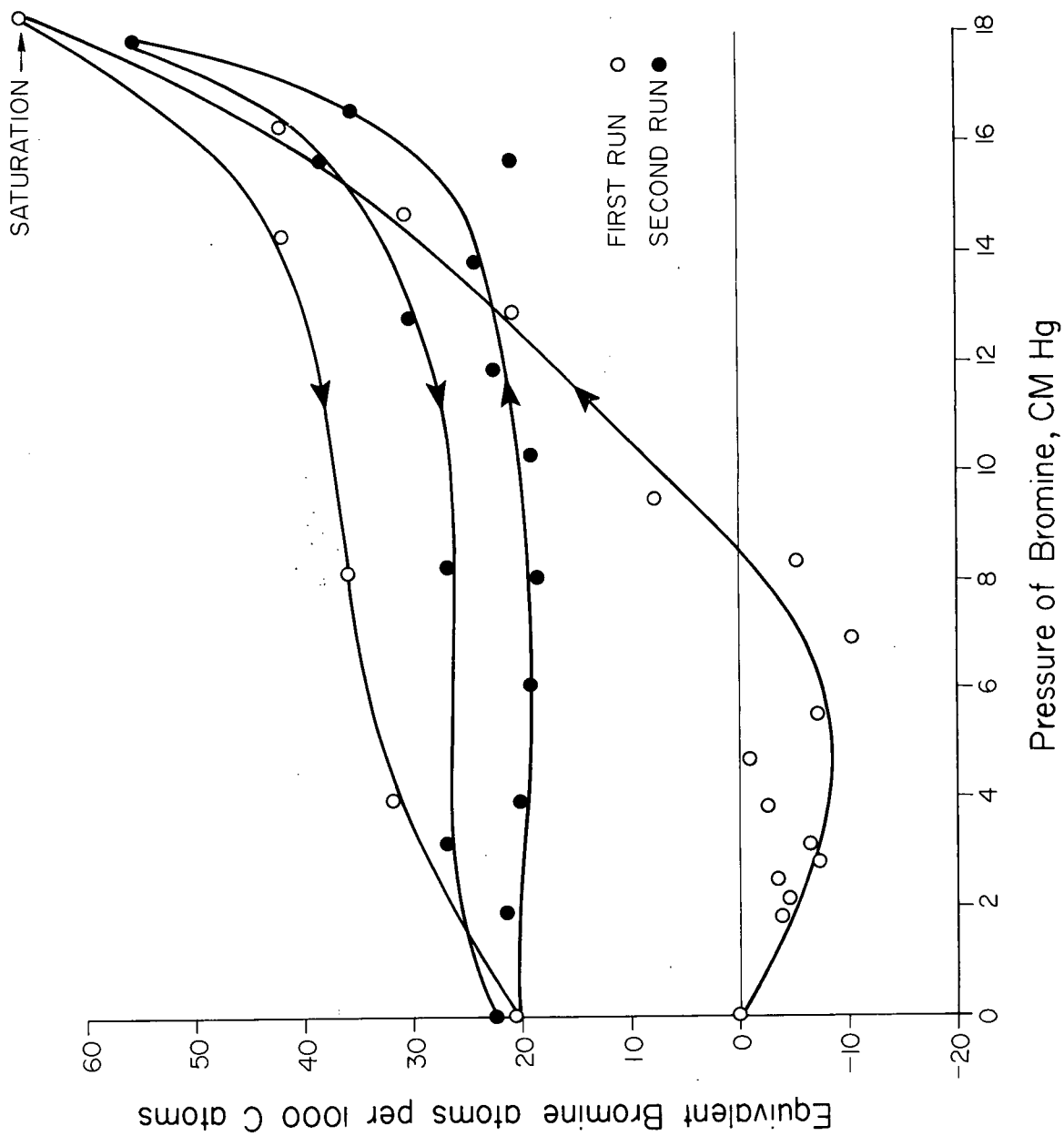


Figure 10: Isotherm of bromine on C_7FeCl_3 at $20^\circ C$

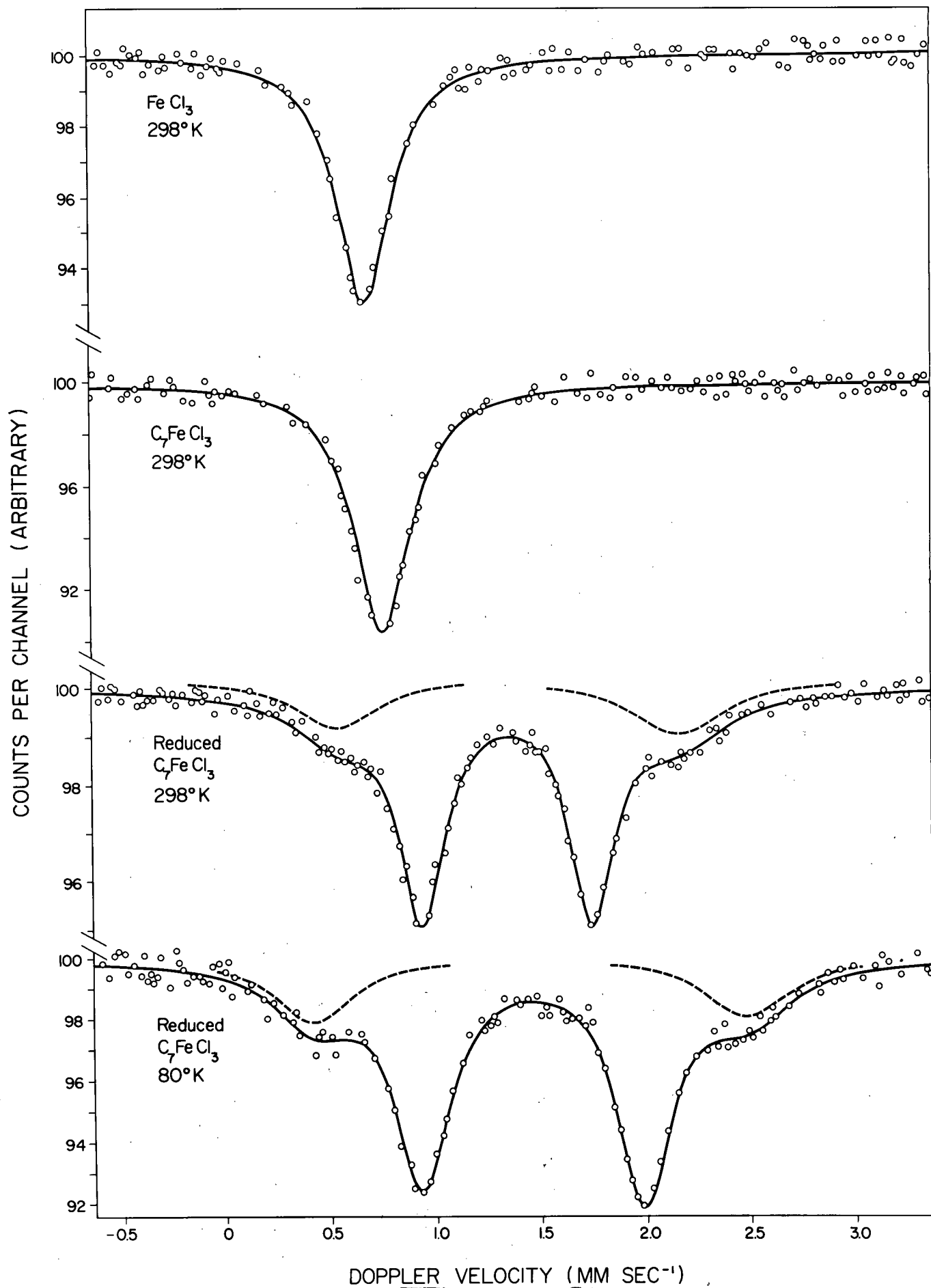
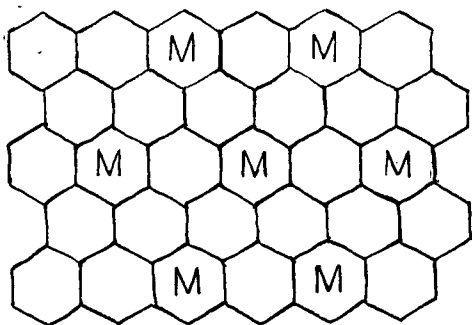


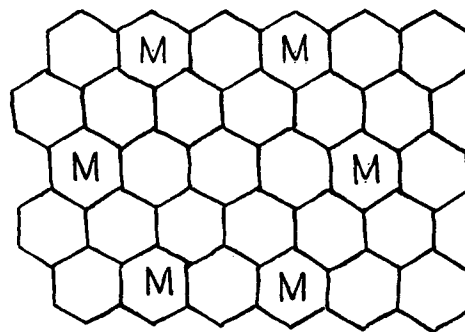
Figure 11: Mössbauer Spectra of FeCl_3 , C_7FeCl_3 , and of Reduced C_7FeCl_3

DISCUSSION:

The isotherms at 300°C and 310°C for the reaction of FeCl_3 with SP-1 show that C_7FeCl_3 is the only observable compound formed between zero pressure and saturation, both on absorption and desorption. It is possible that less concentrated compounds exist over narrower pressure ranges than the pressure increments measured during the isotherm. The isotherm at 350°C raised this possibility for $\text{C}_{12}\text{FeCl}_3$ was formed at this temperature before C_7FeCl_3 . It is, therefore, possible that less concentrated compounds might be observed by running higher temperature isotherms. From the above results it can be seen that the glass bomb preparations succeeded in retaining the maximum uptake of ferric chloride within the graphite. Possible structures that are often postulated for the compositions C_8M and C_{12}M (where M is an adduct and every layer is occupied) (26):



C_8M



C_{12}M

C_7FeCl_3 would result from the above structure for C_8M if the structure were distorted in such a manner that one ferric chloride molecule for every fifty-six carbon atoms was added.

It is interesting that the isosteric heat of intercalation of ferric chloride is of the same order of magnitude as those of bromine, iodine monochloride, and chromyl chloride. These are: 13.0 ± 1.0 kcal/mole for $FeCl_3$ on SP-1, 11.6 ± 0.5 kcal/mole for ICl on SP-1 (4), and 13 ± 0.9 kcal/mole for CrO_2Cl_2 on SP-1 (4). The isosteric heat of intercalation for bromine on SP-1 appears not to have been measured, but it is known to be about 11.7 kcal/mole for Br_2 on natural graphite (27). The significance of these is unknown since the isotherms show hysteresis and are therefore not thermodynamically reversible. In addition it is as yet unknown whether the same composition at different temperatures had the same structure.

The threshold pressures for ferric chloride, iodine monochloride, and bromine on SP-1 are all of the same order of magnitude. These are (relative to saturation): 0.01 for $FeCl_3$ (measured from the 310° isotherm), 0.03 for ICl (4), and 0.05 for Br_2 (4). The maximum uptakes (discounting capillary condensation) are in the same order: C_7FeCl_3 , C_8ICl , and $C_{16}Br_2$. The order of threshold pressures and maximum uptakes shows that ferric chloride enters graphite more readily than iodine monochloride, which in turn enters more readily than bromine. The significance of this variation is as yet unknown. However, one can eliminate several factors that might be expected to influence threshold pressure: for instance,

molecular size cannot be important, since bromine is the smallest of the above three molecules and ferric chloride is the largest. In addition, polarity of the adduct does not seem to be very important, for iodine monochloride is the most polar of the three.

The finding that the threshold pressure for intercalation of FeCl_3 into PG-1 is higher than for SP-1 is in the qualitative agreement with the findings of Hooley, Garby, and Valentin (6) that increased interlayer bonding increases the threshold pressure. The ratio of the threshold pressures of PG-1 to SP-1 at 300°C is 35. For bromination at 20°C it is 8.4 (using a PG-1 sample of the same dimensions). This ratio might be expected to be the same for both reactants, since for each reactant one is comparing the difference in reactivity for two graphites. A possible rationalization is offered. Consider the threshold pressure to arise from two factors: (1) the ease of transfer of electrons from the conduction band to an electronegative adduct, and (2) the ability of the layers to bend aside when a reactant enters the graphite. Qualitatively, it is reasonable that the first should be a function of temperature, for as the temperature rises there will be increasing thermal population of the conduction band of graphite. Thus more electrons will be available for transfer to the entering adduct. The second factor should be much less sensitive to rising temperature until interlayer bonds arising from non-alignment of neighboring crystallites (6) can be annealed out. Heat treatment of graphite to align neighboring crystallites is known not to take place below 2500°C . On this

basis, the threshold pressure of a graphite with relatively few interlayer bonds like SP-1 should be much more affected by temperature than a graphite like PG-1 where interlayer bonding is probably a major factor in determining the threshold pressure. The overall result would be that the ratio of threshold pressures for PG-1 to SP-1 should increase with increasing temperature--as observed. It is, of course, possible that the ratio of threshold pressures for PG-1 to SP-1 varies from reactant to reactant. This could be checked by measuring the ratio for a third reactant at 20°C.

The apparent weight increase of PG-1 on desorption (figure 4) may be explained by postulating that the sample, in analogy to its behavior in bromine (6), split into thin discs at its threshold pressure. Further subdivision continued slowly. As the length of the discs normal to the layer planes decreased, more ferric chloride was intercalated. Hence, the high pressure points of the isotherm are not true equilibrium points--had the sample been left longer slow disc production would have allowed more ferric chloride to intercalate. It appears that the isotherm should be repeated in the future, spending more time on the absorption points above the threshold pressure.

The limited pressure stability range of $C_{12}FeCl_3$ observed in the 350°C isotherm on SP-1 makes it improbable that this product would be recovered from a bomb containing the maximum uptake of C_7FeCl_3 . Yet many investigators (10) (11) (12) (28) have reported compositions from bomb preparations of $C_{10-12}FeCl_3$ after acid washing their preparations. The explanation for the

lower concentrations found by other workers compared to the glass bomb products of this study may lie in their sample flake size and method of sample preparation. The sample of SP-1 used in this study consisted of flakes 20 to 100 microns in diameter (4). The sample used by Cowley and Ibers (12) was 44 microns and less in diameter (-325 mesh). Barker and Croft used a sample of flake size 208 to 295 microns and obtained a 55.5% uptake (same as $C_{10.8}FeCl_3$), but they had ground their sample. This could introduce cracks into the flakes. Rüdorff and Schultz (10) used a 120 to 140 micron sample, but it consisted of Ceylon graphite which has very small crystallites. The point of the sample flake size is that when the sample cools, some $FeCl_3$ will diffuse out from the edges. More ferric chloride would be expected to be lost on cooling from crystals with large amounts of edges per unit weight--ie, from smaller crystals or from crystals that have internal cracks that could release ferric chloride on cooling. Hence, the 44 micron and less flakes of Cowley and Ibers should and do lose more ferric chloride than the 20 to 100 micron crystals of the present study * (they reported 55.5% uptake). Support for this explanation comes from the observation of Cowley and Ibers that heating their 55.5% $FeCl_3$ preparation to 300°C caused the hkl lines of free graphite to disappear. This suggests that the free graphite observed in their

*It is recognized that this statement assumes a uniform distribution of flake sizes for SP-1. A sieve determination showed that the weight percentage greater than 74 microns (+200 mesh) is 30%--exactly the value that would result from a uniform distribution. In addition, the sample used by Cowley and Ibers may have been ground to pass a 325 mesh screen.

preparation was a skin of graphite around the edges of the crystals. When the 55.5% preparation was heated, ferric chloride from the central regions of the crystal expanded into the edges. The existence of a skin of graphite around the edges of the crystals, would also explain the stability of graphite-ferric chloride preparations to acid washing, since the skin of graphite would prevent access of acid to ferric chloride. It is interesting to note that Cowley and Ibers reported that their 55.5% preparation consisted of 17% free graphite, with the remaining 83% being a more concentrated graphite-ferric chloride compound. This would make the more concentrated compound $C_{6.8}FeCl_3$ --approximately the maximum uptake found in the isotherms of this study. Their additional observation that the density of their product (determined by flotation) was not uniform can be explained by the distribution of flake sizes in their sample. The smaller particles which have more edges per unit weight would lose more ferric chloride than the larger particles, and so would be less dense than the larger flakes. A systematic study of the influence of sample size and of sample treatment could confirm the above explanation and form the basis for a future study.

The observation that C_7FeCl_3 resulted from the glass bomb runs in this study regardless of whether the bombs were cooled rapidly by removal of the bomb at $300^{\circ}C$ from the furnace, whether the bomb was cooled at $10^{\circ}C/hour$ for 24 hours, or whether the graphite-ferric chloride was held at $300^{\circ}C$ for 15 minutes while the ferric chloride pressure was reduced to

zero shows that the amount of ferric chloride retained by the graphite is insensitive to the rate of pressure or temperature reduction, at least within the ranges studied. However, the isotherms all show that if the pressure is reduced in several steps while the graphite is held at 300°C, most of the ferric chloride will sublime out of the graphite to leave a typical residue compound with mole ratio (C/FeCl₃) of 20 to 50. It should be noted that the total desorption time on an isotherm was of the order of 250 to 300 hours, with about 100 hours spent at zero pressure.

The Mössbauer spectrum of C₇FeCl₃ at room temperature (table 1) consists of a single unsplit peak at 0.78 mm/sec relative to sodium nitroprusside. This is slightly shifted to higher velocity from the single peak of crystalline ferric chloride at 0.69 mm/sec. This similarity of the Mössbauer spectra is in accordance with Cowley and Ibers' (12) observation that the layers of ferric chloride in graphite are only slightly distorted from their structure in crystalline ferric chloride, since the retention of the single peak shows that the nuclear environment of iron is but slightly altered in C₇FeCl₃ from its octahedral environment in anhydrous ferric chloride. The shift of the peak to higher velocity in C₇FeCl₃ implies a lower s-electron density than in ferric chloride itself (29). This effect can be explained if iron 3d orbitals receive electrons, thus deshielding the 3s orbitals and decreasing the total s-electron density at the nucleus. This is in agreement with an earlier study (13) based on Hall coefficient measurements on graphite-ferric chloride which showed that it

is a p-type compound, ie., electron transfer is from the graphite to the ferric chloride. However the ionic structure $C_n^{+}.3FeCl_3$ suggested by Hennig (13) is clearly not in accordance with the observation of a single Mössbauer peak at a velocity characteristic of ferric iron. The observation that the Mössbauer peak of C_7FeCl_3 at $80^{\circ}K$ is at lower velocity than the peak for anhydrous ferric chloride at that temperature (table I) is ambiguous. Further study will be necessary before attempting an interpretation. A Hall coefficient measurement at $80^{\circ}K$ would be helpful, since the isomer shifts of C_7FeCl_3 and $FeCl_3$ at $80^{\circ}K$ in table I seem to indicate little or no electron transfer from graphite to ferric chloride.

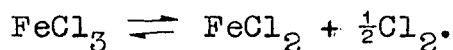
X The appearance of two quadrupole-split peaks with a common isomer shift of 1.46 mm/sec at $80^{\circ}K$ and the disappearance of the peak at 0.08 mm/sec at $80^{\circ}K$ when C_7FeCl_3 was hydrogenated confirms the reduction of intercalated $FeCl_3$ to $FeCl_2$ (table I).

The product's weight loss was slightly higher than that required for complete reduction of $FeCl_3$ to $FeCl_2$. The extra weight loss was probably due to sublimation of some $FeCl_2$ out of the graphite. The fact that this preparation was washed with 6N HCl indicated that the iron must still be in the graphite rather than on the surface. The additional fact that the X-ray powder photograph was similar to the original C_7FeCl_3 (but not identical) also suggests the iron chloride is within the graphite rather than on the surface. The closeness of the isomer shift of the hydrogenated C_7FeCl_3 to that of anhydrous ferrous chloride (24) implies that there is little or no

electron transfer from the graphite to the ferrous chloride.

The two inner peaks (see figure II) have the same quadrupole splitting as anhydrous FeCl_2 (24) (table I). Hence it is reasonable to suggest that the bulk of the iron in the graphite is in sites corresponding to those of the ferrous chloride lattice. The two outer peaks have about double the quadrupole splitting of anhydrous FeCl_2 (24). The origin of these peaks will require further study.

The Mössbauer spectrum of the $\text{C}_{12}\text{FeCl}_3$ prepared in stainless steel bombs (table I) results from the superposition of the Mössbauer spectra of C_7FeCl_3 and the hydrogenated C_7FeCl_3 . Hence the product prepared in the stainless steel bombs contains both ferric and ferrous iron. An explanation is offered. Ferric chloride is known to be in equilibrium with about 3 cm Hg pressure of chlorine at 300°C (30) according to the equation:



If intercalated ferric chloride is also in equilibrium with chlorine, then some chlorine from ferric chloride near the edges of the graphite might be expected to escape from the crystals. The chlorine could then react with the iron in the walls of the bomb to form ferric and ferrous chloride. As the ferric chloride pressure in the bomb is reduced to zero by cooling the bomb then any free chlorine will react with the ferrous chloride to re-form ferric chloride, both in the body of the bomb and in the graphite. But some of the chlorine originally evolved was lost by reaction with the walls of the bomb. Hence some of the ferrous chloride in the graphite

cannot be re-oxidized to ferric chloride. It is reasonable that there should be a mixture of ferric and ferrous chlorides, for chlorine from intercalated ferric chloride near the centre of the crystal would be expected to have more difficulty in leaving the graphite than chlorine from ferric chloride at the edges of the crystals. Ferrous chloride would not on the above basis be predicted to be found in a product prepared in a glass reaction vessel since chlorine would not be removed by reaction with the walls. Hence, as the glass bomb products cooled, they would take up the chlorine they had originally evolved. Also, it is unreasonable to suggest that the origin of the ferrous chloride was in the body of the bomb and that FeCl_2 entered the graphite at 300°C since the vapor pressure of ferrous chloride becomes measureable only above 600°C (31).

The above explanation suggests that the reduction of C_7FeCl_3 may not have required hydrogen: merely heating the C_7FeCl_3 to 375°C in a stream of any unreactive gas might have sufficed to carry off all the chlorine in equilibrium with FeCl_3 in the graphite. This possibility is being checked.

It is interesting that the threshold pressures for bromine and iodine monochloride intercalation are slightly higher in $\text{C}_{64}\text{CrO}_2\text{Cl}_2$ and $\text{C}_{100}\text{CrO}_2\text{Cl}_2$ than in pure graphite (4). It will be recalled that bromine does not intercalate $\text{C}_{32}\text{CrO}_2\text{Cl}_2$ and that the threshold pressure for ICl intercalation into $\text{C}_{32}\text{CrO}_2\text{Cl}_2$ is about 0.4 cm Hg (4). The interpretation of the raised threshold pressures is not clear, for either or both of the two factors mentioned below could be responsible. It is possible that the action of chromyl chloride is to remove

electrons from the conduction band of graphite so as to make electrons less available to entering Br_2 or ICl molecules. This action might be expected to be a function of chromyl chloride concentration, provided CrO_2Cl_2 takes up about the same number of electrons per molecule in all stages of its reaction. In addition it is possible that the action of chromyl chloride is to bind the graphite layers together. On the basis of the present data it is not possible to decide which if either of these two factors is important.

The isotherms of Br_2 , ICl and CrO_2Cl_2 on C_7FeCl_3 show that the threshold pressures for all three have been raised above their values in the pure graphite--for chromyl chloride, above saturation. Again, it is not clear how to interpret the raised threshold pressures. It is interesting that in spite of the large weight increases during the ICl and Br_2 isotherms, there are no definite plateaus. It is possible that much of the observed weight increase resulted from capillary condensation. This could be true if the C_7FeCl_3 had a more porous structure than the original graphite. Studies using absorbents which do not intercalate graphite could test this possibility.

The weight decrease observed in the initial stages of reaction of Br_2 with C_7FeCl_3 is interesting. In addition, the failure to observe uptake when a second isotherm was run on the residue is puzzling. However, these results will have to be confirmed in a future study before any firm conclusions can be drawn.

The studies of the reaction of chromyl chloride with graphite showed that this system is more complex than previously realized. It appears that the isotherm of chromyl chloride on graphite is time-dependent, ie., the uptake at one pressure is not independent of the length of time the sample has been left at a lower pressure. Indeed, if a sample is left sufficiently long (2 days with the chromyl chloride pressure below the usual threshold pressure of 0.4 cm Hg) below the threshold pressure, no uptake is observed. In addition, the observations reported in "Experimental" suggest that different natural crystals of graphite show large variations in their reactivity with chromyl chloride. Again, further study of the chromyl chloride-graphite system is needed.

The final observation that only $C_{40}CrO_2Cl_2$ results when chromyl chloride is reacted with graphite at $100^{\circ}C$ in the absence of air and water is not in accordance with Croft's report (8) of $C_{16}CrO_2Cl_2$. Croft reacted graphite with chromyl chloride at $100^{\circ}C$, but apparently took no precautions to exclude air and water. Hence, it is possible that some of the uptake he reported consisted of hydrolysis products of chromyl chloride (such as CrO_3 , Cr_2O_3 , etc.) insoluble in CCl_4 (which he used to wash his preparations).

CONCLUSIONS:

- (1) Ferric chloride reacts with graphite to form two compounds, C_7FeCl_3 and $C_{12}FeCl_3$.
- (2) Electrons are transferred from graphite to ferric chloride. All of the ferric chloride is in the same oxidation state.
- (3) Ferric chloride intercalated in graphite is reduced to ferrous chloride in hydrogen at $375^{\circ}C$.
- (4) The threshold pressure for intercalation of bromine, iodine monochloride, or chromyl chloride is higher on graphite-ferric chloride or graphite-chromyl chloride than on the original graphite.

Table I. Isomer shifts and quadrupole slittings for FeCl_3 , FeCl_2 , and their interlaminar graphite compounds. All isomer shift values are relative to NBS Sodium nitroprusside, NBS standard material #725. See figure 11.

Compound	T, °K	Isomer shifts mm/sec	Quadrupole slittings mm/sec
FeCl_3	298	0.69 ± 0.01	-
		0.63 ± 0.05^a	-
	80	0.82 ± 0.01	-
		0.83 ± 0.05^a	-
		0.815 ± 0.005^b	-
C_7FeCl_3	298	0.78 ± 0.01	-
	80	0.80 ± 0.01	-
Reduced	298	1.35 ± 0.01	0.818 ± 0.005
C_7FeCl_3			1.635 ± 0.005
	80	1.46 ± 0.01	1.065 ± 0.005
			2.077 ± 0.005
FeCl_2^c	290	1.34 ± 0.05	0.80 ± 0.02
	78	1.48 ± 0.07	1.01 ± 0.02
$\text{C}_{12}\text{FeCl}_3$ from Stainless Steel Bomb		Resolved by computer into Lorentzians matching the peaks of C_7FeCl_3 and reduced C_7FeCl_3 above.	

^a Reference 34

^b Reference 33

^c Reference 24

BIBLIOGRAPHY

- (1) Rüdorff, W. Z. Anor. Allgem. Chem. 245, 383 (1941).
- (2) Herold, A. Comptes Rendus 239, 591 (1954).
- (3) Reyerson, L.H. et al. J. Phys. Chem 61, 1334 (1954).
- (4) Hooley, J.G. Can. J. Chem 40, 745 (1962).
- (5) Rüdorff, W. Adv. Inorg. Nucl. Chem and Radio chem 1, 251 (1959).
- (6) Hooley, J.G., W.P. Garby, and J. Valentin. Carbon 3, 7 (1965).
- (7) Rüdorff, W., V. Sils, and R. Zeller. Z Anor. Allgem. Chem 283, 299 (1956).
- (8) Croft, R.C. and R.G. Thomas. Nature 168, 32 (1951).
- (9) Thiele, H. Z. Anor. Allgem. Chem. 207, 304 (1932).
- (10) Rüdorff, W. and H. Schultz. Z. Anor. Allgem. Chem 245, 121 (1940).
- (11) Croft, R.C. and J.A. Barker. Australian J. Chem 6, 302 (1953).
- (12) Cowley, J.M., and J.A. Ibers. Acta Crystallographia 9, 421 (1956).
- (13) Dzurus, M.L. and G.R. Hennig. J. Amer. Chem. Soc 79, 1051 (1957).
- (14) Hooley, J.G. Carbon 2, 131 (1964).
- (15) Hooley, J.G. and W.P. Garby. Unpublished Results.
- (16) Hooley, J.G. Can. J. Chem. 35, 374 (1957).
- (17) Hooley, J.G. Can. J. Chem. 35, 1414 (1957).
- (18) Kangro, W. and H. Burnstoff. Z. Anor. Allgem. Chem 263, 316 (1950).
- (19) Rüdorff, W. and A. Landel. Z. Anor. Allgem. Chem 293, 327 (1957).
- (20) Bartlett, M.W., J.G. Hooley, B.V. Liengme, J. Sams, and J. Scott. To be published.
- (21) Grant, G.L. B. Sc. Thesis (1967) University of British Columbia.

- (22) Gross, R. Ph.D. Thesis (1962) Université de Nancy, France.
- (23) Bartlett, M.W. B.Sc. Thesis (1965). University of British Columbia.
- (24) Ono, K., A. Ito, and T. Fujita. J. Phys. Soc. Japan. 19, 2119 (1964).
- (25) Liengme, B.V., M.W. Bartlett, J.G. Hooley, and J.R. Sams
Submitted for publication in Phys. Rev. Letters.
- (26) Hennig, G.R. Progress in Inorganic Chemistry 1, 153 (1959)
- (27) Hooley, J.G. Can. J. Chem. 37, 899 (1959)
- (28) Lazo, R.M. and J.G. Hooley, Can. J. Chem. 34, 1574 (1956)
- (29) Greenwood, N.N. Chemistry in Britain, 56 (1957).
- (30) Maier, C.G. "Vapor Pressures of the Common Metal Chlorides
and a Static Method for High Temperatures", Page 53.
U.S. Bureau of Mines, Technical Papers, 360 (1925).
- (31) Maier, C.G. ibid, page 31.
- (32) Asher, R.C., and S.A. Wilson. Nature 181, 409 (1958).
- (33) Krocher, C.W. Phys Lett. 24 A, 93 (1967).
- (34) De Benedetti, S., G. Lang, and R. Ingalls. Phys Rev
Letters 6, 60 (1961).

ERRATA:

Page 1, line 10: substitute "complete" for "compleate."

Page 5, line 12: substitute "subdued" for "sudued."

Page 14, line 2: insert "forms" between " $C_{12}FeCl_3$ " and
"in the range. . ."

Page 16, last line: add "for C_7FeCl_3 ." at end of sentence.

Page 23, paragraph 2, line 2: insert "because" between
"perhaps" and "of varying amounts"

Page 24, line 14: substitute "succeeded" for "suceeded."

Page 31, line 2: formulatis " $C_n^+ \cdot FeCl_3^- \cdot 3FeCl_3$."

line 15: substitute "0.80 mm/sec" for "0.08 mm/sec."

line 19: substitute " $FeCl_3$ " for " $FeCl_2$."

Page 30, line 25: substitute "shielding" for "deshielding."

Page 39, line 11 (reference 29): 1967 rather than 1957.