RADIOCHEMICAL STUDIES on GRAPHITE FERRIC CHLORIDE

BY

ROBERT MARTIN LAZO

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ABSTRACT

Graphite ferric chloride, $C_{12}FeCl_3$, was prepared by heating anhydrous ferric chloride with graphite at 305°C. The purified compound containing 53% ferric chloride was not attacked by hot 6N hydrochloric acid or 6N sodium hydroxide solutions. X-ray diffraction measurements gave a powder pattern which was distinctly different from that of either graphite or ferric chloride and from which it was apparent that no free ferric chloride existed in the compound. The separation of the graphite layer-planes was increased from 3.36 to 9.4Å by the intercalation of the ferric chloride molecules.

Tests for exchange between $C_{12}FeCl_3$ and Fe^{+++} ion were made using radioactive Fe^{59}. In no instance was any measurable exchange observed. The compound was subjected to neutron irradiation and the Szilard-Chalmers yield of separable activity calculated and identified. The separated portion contained less than 1% of the total activity and consisted of Fe^{59}, P^{32} and S^{35}, free of detectable radiation decomposition products. The active Fe portion was separated by ether extraction.

The lack of exchange and the low Szilard-Chalmers yield are both attributed to the formidable steric hindrance effects which result from the configuration of the "stacked layers" structure for graphite ferric chloride.

ACKNOWLEDGEMENTS

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INTRODUCTION

Carbon itself is a refractory, non-volatile, insoluble solid, and gives rise to lamellar compounds which are insoluble, non-volatile and often unstable solids about which classical chemical methods give very little information. X-ray studies have proved particularly fruitful, and most of the information concerning the structure of solid carbon, and its lamellar compounds has been determined from X-ray diffraction measurements.

Carbon, in the form of diamond, belonging to the cubic system, was one of the earliest crystals to be investigated by X-rays(2). The essential point of the space lattice structure for diamond, is that every atom of carbon is surrounded by four other atoms situated at the corners of a regular tetrahedron. The distance between the centers of two adjoining atoms is 1.54Å , which corresponds very closely to the distance between two carbon atoms attached to each other by a single covalent bond in aliphatic organic compounds. This agreement, together with the fact that each carbon atom in diamond has four others situated round it at the corners of a regular tetrahedron, suggests that every atom is joined to four others by covalent linkages. A diamond crystal may then, be regarded as a macromolecule of carbon. Its hardness can be ascribed to the strength of the chemical bonding of the atoms and its uniformity in all directions throughout the crystal.

The physical properties of the other allotropic form
of carbon viz., graphite, of the hexagonal system, are
quite different from those of diamond. These differences
are found to correspond to important changes in the internal
structure of the crystal.

Although graphite is so obviously crystalline, its
opaque cha racter and the rarity of well developed crystals
restrict considera bly the crystallographic information
which can be obtained by optica l methods. The lattice
s tructure which first received wide acceptance was deduced
in 1924 by J.D. Bernal (1) and confirmed by C. Mauguin
(1926) (12) and by H. Ott (1928) (16).

The carbon atoms are arranged in flat layers each
having a hexagonal honeycomb-like structure. These are
stacked parallel to each other in such a way that half
the atoms in one layer lie normally above half the a toms
in the layer beneath. Alternate layers lie, atom for atom
normally above each other. The carbon atoms in the layers
are spaced center to center at a distance of 1.415 Å
compared with a spacing of 1.54 Å in the diamond lattice.
The spacing between adjacent layer-planes of graphite is
3.36 Å . The carbon atoms within the layer-planes therefore
are bonded together by powerful covalent valency forces,
more powerful tha n those in the diamond. The four valences
of each carbon atom are used to form bonds with its three
neighbors, and the giant layser molecule resonates among
many va lence-bond structures in such a way that each
carbon-carbon bond achieves one-third double-bond character.

This arrangement corresponds very closely to the six- membered rings formed in benzene, naphthalene and other aromatic hydrocarbons. Indeed, in his review of recent work on the similiarity of the graphite electron structure with that of aromatic compounds (6), Hofmann has stated, "No sharp boundary is found. The intermediary stages of graphite nuclei in coal and in various charcoa ls constitute a gradual cha nge from aromatic compound to crystalline graphite". However the resonance system in the graphite layer-planes is so degenerate that odd electrons behave more like metallic electrons and account for the electronic conductivity of graphite, which with certa in pure specimens is twice that of mercury. The electrical conductivity in a direction parallel to the layer-planes is much greater than in a direction at right angles to it.

The hexagona l layers of carbon molecules are separated by a distance so large (3.36 Å) that there can be no covalent bonds between them, and the superimposed layer molecules are held together only by weak van der Waals forces (17). The layer-lattice set up for graphite accounts for the cleavage which occurs so easily between the separate layer-planes in the crystal, and the use of graphite as a lubricant depends on this ability of one plane of atoms to slide easily over another.
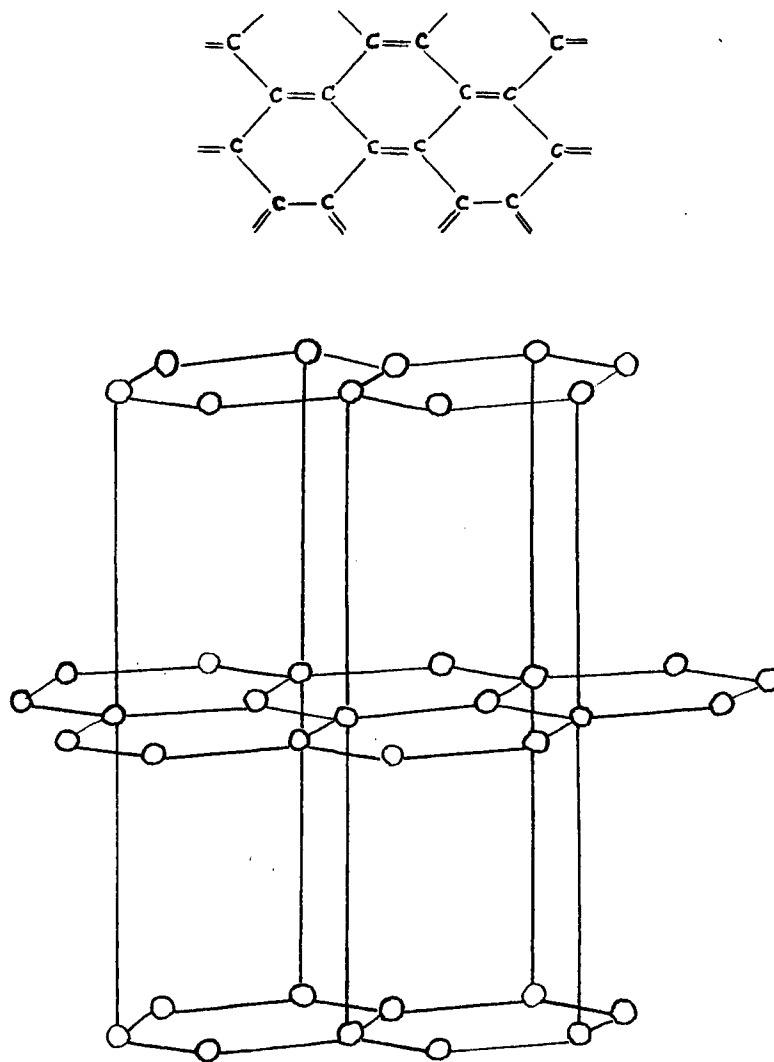
Figure 1.   The arrangement of carbon atoms
in the graphite crystal.

The structure of the graphite crystal lattice appeared to be definitely established until D.S. Laidler and A. Taylor (10) in 1940 pointed out that this structure does not account for some faint lines which occur in the X-ray powder photographs of many specimens of graphite. Another form of graphite present to about 10% is suggested. Instead of the alternate planes being normally above one another, a third plane is inserted which is symmetrically related to the planes above and below.

Figure 2. The two ways of stacking the hexagon layer-planes in the graphite lattice.

The graphite lattice structure with its powerful covalent bonds within the layer-planes and the relatively weak bonding forces between the layer-planes offers an explanation of

the interesting anisotropic properties both physical and chemical, associated with graphite crystals. Observations on the swelling of graphite electrodes and the intumescence of graphite, led to the discovery that certain molecules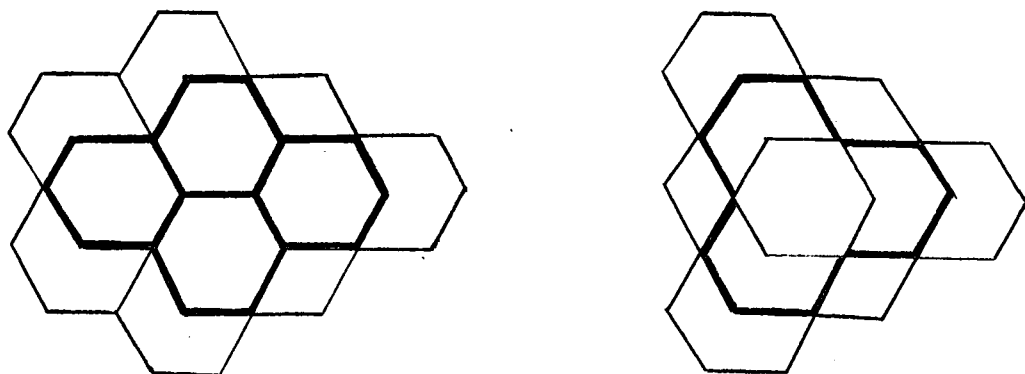 and/or ions could penetrate between the layer-planes of the graphite lattice to form more or less stable structures. This swelling, as pointed out by H. Thiele (33), occurs with highly crystalline forms of graphite and occurs exclusively along the C axis of the hexagonal flake.

<u>Graphite Salts</u>: The action of concentrated acids in the presence of a suitable oxidizing agent, has been shown to bring about the formation 6f blue graphite salts (7) (23). Each hexagon layer-plane becomes a macro positive ion with a charge equal and opposite to the number of negative ions bonded to it. When graphite is treated with boiling sulfuric acid in the presence of a few drops of nitric acid, the iridescent blue graphite bisulfate results.

$$\text{Graphite} + nH_2SO_4 + n/20 \rightarrow \text{Graphite}^{n+}(HSO_4^-)n + \tfrac{1}{2}H_2O$$
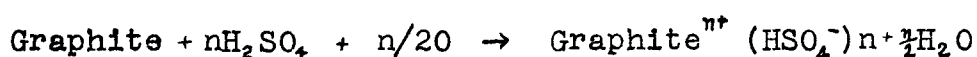
The compound containing the maximum amount of intercalated bisulfa te ion and sulfuric acid corresponds to the idealized stiochiometric composition $C_{24}HSO_4 \cdot 2\ H_2SO_4$.

The addition of a small quantity of water to the sulfuric acid, even from exposure of the acid to the atmosphere brings about the decomposition of the blue graphite into the original graphite. X-ray examination of a specimen of graphite bisulfate suspended in pyrophosphoric acid

(6)

showed that the intercalation of the sulfuric a cid had increased the inter layer-plane spacing of the graphite from 3.36 Å to 7.98 Å (19).

Besides the bisulfate, graphite forms other similar compounds. H.L. Riley, in his review of "Lamellar compounds of carbon" (19) describes the graphite salts nitrate, per-chlorate, biselenate, phosphate, pyrophospha te and arsenate, all prepared and characterized by Rüdorff and Hofmann (23).

Graphite Monofluoride: (27) Graphite combines with fluorine at one atmosphere pressure and a temperature of 420°C. to form a grey hydrophoBic solid the composition of which is $(CF)_n$. The constant composition, the grey color and the low electrical conductivity, which is only one-hundred-thousandth that of graphite, all suggest that graphite mono- fluoride is a chemical campound. The fluorine atoms are arranged in six parallel planes between each pair of carbon layer-pla nes which a re spaced at 8.17 Å . Rüdorff has recently announced the preparation of a new graphite-fluorine com-pound (24) tetracarbon monofluoride $(C_4F)_n$. The compound is not a ttacked by dilute acids or alkali even on heating although concentrated sulfuric acid above 100°C slowly dec-omposes it.

Brom-graphite: A pecular bromine adsorption complex of graphite has been produced (21) by shaking a suspension of graphite in cold concentrated sulfuric acid with bromine. The graphite samples will take up roughly one atom of

(7)

bromine to each eight atoms of carbon and give it up again completely on standing in the air. The X-ray analysis of brom-graphite showed a carbon layer-plane spacing of 7.05 Å.

Alkali-graphite: When graphite is heated with potassium, rubidium or cesium in an evacuated tube, a blue-black alkali-graphite compound is produced. Shaking the compound in mercury converts it to graphite. It was also found that the adsorption of potassium vapor occured in a stepwise manner, indicating the formation of more than one compound. Schleede and Wellmann (28) determined from X-ray studies that for the C_8K compound, each potassium atom lay normally over the center of every second carbon atom hexagon of the basal planes. $C_{16}K$ has a layer of potassium atoms in every second inter-layer-plane space in the graphite lattice. These substances were shown to be quite different from ordinary alkali metal carbides because only hydrogen and no trace of hydrocarbon was evolved when they reacted with water. The heat of formation of C_8K or $C_{16}K$ using excess potassium, was determined to be about 1500 cal./gm. atom of carbon (4).

Graphitic oxide: Samples of graphitic oxide have been prepared by treating graphite that had been previously washed with hydrochloric acid, with concentrated sulfuric acid and nitric acid in the presence of potassium chlorate (26). After the product has been dried under vacuum over potassium pentoxide the acid groups can be determined by methylation

(8)

and acetylation. However, in no case has a fixed stio-
chiometrical relationship been found, as analyses for C:O
varies between 6:1 and 6:2.5. Further studies of the crystal
structure have indicated that the carbon layers display a
hydroaromatic character.

It is interesting to note the close parallelism between
the chemistry of the graphite compounds that have been men-
tioned and that of the triarylmethyls (18). This is indicated
by the existence of the graphite salts, graphite monofluoride,
the alkali graphites and graphite oxide, all of which appear
to be definite compounds. The triarylmethyls also form
alkali salts, halides and peroxides and in general show the
same amphoteric properties as do the hexagon layer-planes
of the graphite crystal lattice. This is not surprising,
for considering one carbon atom in a layer-plane, it will
be seen that its three valency bonds are connected each to
an aromatic grouping of carbon atoms and that these three
bonds are co-planar, like those in triphenylmethyl. The
stability of the triphenylmethyl free radical has been expl-
a ined by assuming that the odd electron on the central
carbon a tom resonates among many of the aromatic carbon
atoms in the molecule. This is a very similar type of
resonance to that occuring in graphite.

A. Graphite ferric chloride:

Perhaps the most interesting of the graphite
compounds reported to date, is the surprisingly sta ble
graphite ferric chloride, which appears to fall into a

different category, as no similar compound is formed by the triarylmethyls.

Graphite ferric chloride was prepared and characterized by W. Rüdorff and H. Schulz (25) in 1940 and is reviewed in the U. S. publication F.I.A.T. (1948) (22).

When graphite is heated to 200°C. and above with two or three times its own weight of anhydrous ferric chloride in a sealed tube, the amount of free ferric chloride decreases. The ferric chloride which does not react can be sublimed off or extracted in dilute acid solutions, leaving an apparently homogeneous green to matt black reaction product which has increased in weight up to 200% of the weight of the original graphite.

Specimens prepared between 180° and 300°C. contain between 72% and 60% of ferric chloride, which is equivalent to 1 FeCl : 5.5-9 C atoms. Using reaction temperatures between 325° and 400°C, the ferric chloride content falls to between 37% and 31% i.e. 1 FeCl : 23-29 C atoms, and between 400° and 500°C. the product contains only 5% ferric chloride. This is completely expelled only at a temperature above 500°C.

At 309°C. the graphite ferric chloride complex showed a pronounced intumescence accompanied by the evolution of $FeCl_3$ vapour. This phenomenon was repeated again at 409°C. and there then remained a grey pulverulent substance which still contained about 5% ferric chloride.

Rüdorff and Schulz found that part of the ferric chloride could be extracted from the complex with water or dilute acids or with alcohol, ether, benzene, etc. When extracted in

this way the graphite ferric chloride prepared below 309°C.
left a product containing about 56% ferric chloride no matter
what solvent was employed and independently of the original
graphite crystal form. This value of 56% ferric chloride cor-
responds to about one molecule of $FeCl_3$ to ten C atoms. Treated
in the same way a specimen prepared between 310 and 400 degrees
centigrade gave a product containing 31% ferric chloride or one
$FeCl_3$ molecule to thirty C atoms. The ferric chloride remaining
in the complex after the extraction was found to be extraordi-
narily unreactive and specimens of the compound were scarcely
attacked by hot dilute acid or alkali. Reducing agents such as
hydrazine and sulfurous acid were found to be without appreci-
able action. Oxidizing agents such as concentrated nitric acid
or not concentrated sulfuric acid however, decomposed the complex.

The properties of graphite ferric chloride and the
stepwise decrease in ferric chloride content, suggested the
existence of two compounds and this was confirmed by X-ray
diffraction measurements. The powder photographs of specimens
containing 56-72% ferric chloride showed pronounced differ-
ences from those of specimens containing 30-37% of the
metallic salt. The diffraction patterns were all distinctly
different from those of either graphite or ferric chloride.
Rüdorff confirmed from X-ray diffraction measurements, that
the spacing between the layer-planes in the graphite had
been increased from 3.36 to 9.4 Å by the penetration of
ferric chloride molecules. This agreed with the increase
in volume of a single crystal to about 2.5 times observed
microscopically and from density measurements.

It is known that anhydrous ferric chloride crystallizes in a layer lattice. The iron ions form a regular hexagonal network above and below which there is a parallel triangular net plane of chloride ions. The dimensional requirements of these layer-planes along the C axis is about 5.8 A . The question arises as to how far the limits of the ferric chloride content found by chemical analysis viz. 1 $FeCl_3$: 5.5C to 1 $FeCl_3$: 9C can be correlated with the suggested crystal structure for graphite ferric chloride. Rüdorff states that this requires an upper limit of 1:6.02 for the $FeCl_3$:C ratio, and that somewhat higher value is due possibly to capillary condensation. The compound with the highest ferric chloride content probably has a hexagonal packing of the ferric ions, and when the excess of ferric chloride is removed by washing the ferric ions take up a triangular packing i.e. one in which alternate ferric ions have been eliminated from the hexagonal arrangement. In the limiting case with the removal of half the ferric ions to form the triangular arrangement, the ratio of $FeCl_3$:C would become 1:12.04. In the work done by Rüdorff and Schulz in 1940, the ratio of 1:10.4 was reported for washed specimens of graphite ferric chloride. One sample after being boiled with 10% H_2SO_4 for twenty-four hours gave the ratio 11.9.

Vapour pressure measurements indicated that the ferric chloride taken up by the graphite in excess of about 56% was loosely bound and probably only served to fill holes in the large mesh network of the more firmly bound ferric chloride molecules.
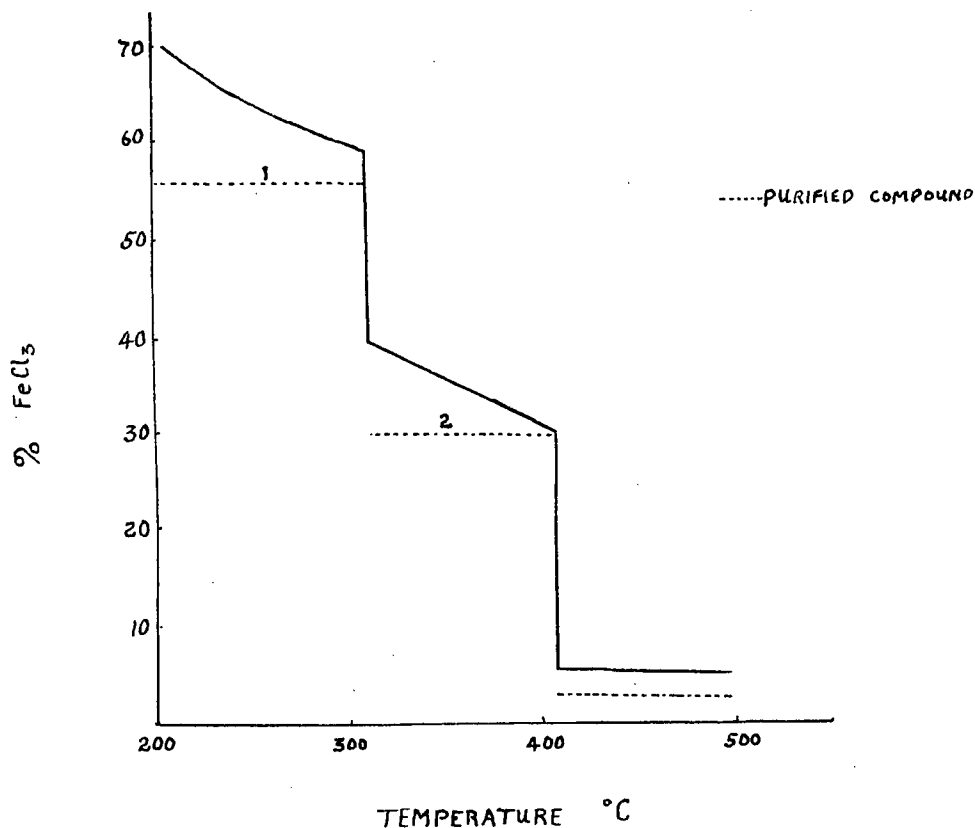
Figure 3-

The effect of temperature on Graphite ferric chloride.

Figure 3. shows the change in the amount of inter-

calated ferric chloride with temperature, as illustrated

by Rüdorff. In the compound prepared below $309°C$. the

ferric chloride has penetrated between all the layer-planes

of the graphite lattice. When this compound is heated to

$309°C$. and above there is a sudden evolution of ferric

chloride as these molecules are forced from between every

alternate pair of layer-planes of graphite. The dotted lines

represent the purified compounds, 1)with ferric chloride

between a 11 the graphite layer-planes, and 2)with the

intercala   tion of ferric chloride only between every

second pair of layer-planes. It will be noted that between 200 and 309°C. temperature has no effect on the percentage of ferric chloride held by the graphite in the purified fully intercalated compound. The same is true for the second compound between the temperature of 309 and 409°C. Above 409° the percentage of ferric chloride drops again leaving only about 5%. Figure 4. shows the layer-plane sequence of the two compounds.

$C_{30}FeCl_3$ $C_{12}FeCl_3$

Figure 4-

The layer-plane sequence of Graphite ferric chloride.

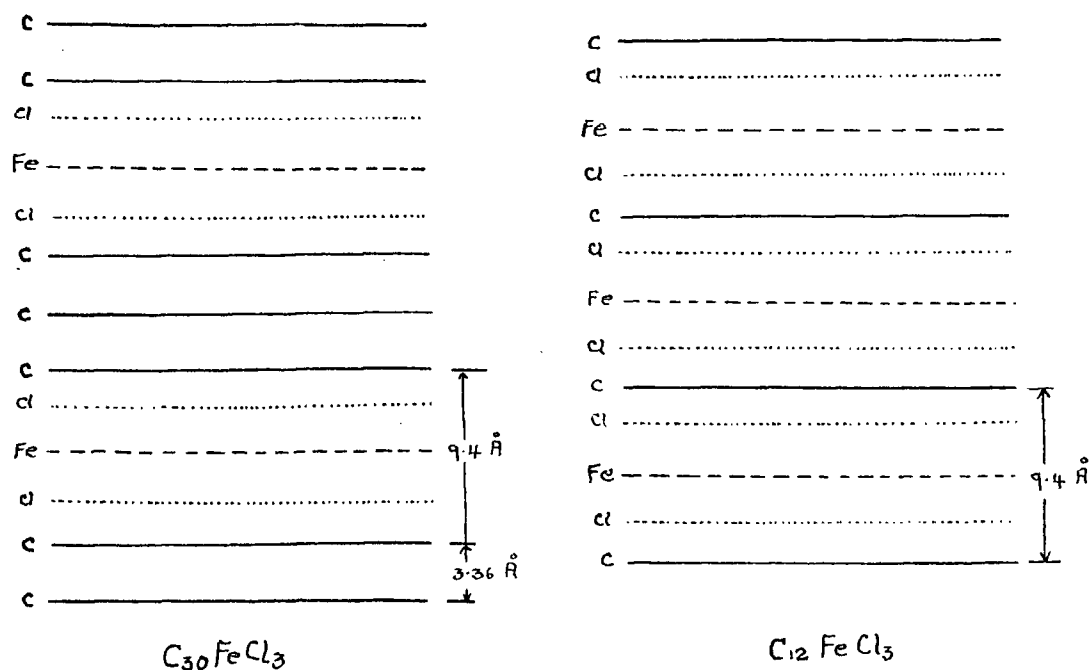The particular stability of the graphite ferric chloride compounds has necessitated some explanation of the type of bonding they exhibit. As has been mentioned previously, the strongly bonded carbon atom layer-planes

of the graphite lattice are held together only by weak
van der Waals forces. The extreme inactivity exhibited
by graphite ferric chloride, in which the graphite layer-
planes have been separated from 3.36 to 9.4 Å , makes
it seem quite unlikely that the bonding of the ferric chloride
in the compound is of the same type. Rüdorff has found that
the magnetic moment of the Fe^{+++} ions in the compound is
the same as that of Fe^{+++} in $FeCl_3$ and concludes that co-
valent bonding of the Fe-C type is out of the question (22).
He suggests instead, that there is a polarization of the
conductivity electrons of the carbon layer-planes toward
the central layer of iron atoms but that these remain
essentially ionic. One can then imagine some degree of
electrovalent bonding of the chlorine ions to the macro
positive ion layer-planes.

In view of the nature of the bonding of the ferric
ions and the configuration of atoms about them in the
graphite ferric chloride structure, it seemed that an in-
vestigation of the possibility of exchanging these ions
or of ejecting them from the lattice by Szilard Chalmers
reaction, would be of interest and perhaps further eluc-
idate the structure of the compound.

2. RADIOCHEMICAL THEORY

Nuclear chemistry is a field of activity as old as nuclear physics. The workers in the late nineties made studies of the possible influence of chemical binding on radioactive decay and searched among the elements for those displaying radioactiveproperties, with the result that a number of new elements were discovered, existing only in radioactive forms. Nuclear science remained predominantly in the hands of physicists, however, in spite of the vast chemical implications of developments in nuclear transmutation and artificial radioactivity that had made available radioactive forms of all of the chemical elements.

With the developments in "modern alchemy", born with the emergence of the uranium chain-reacting pile, chemists of the world began to play a more prominent role in nuclear research. Today nuclear chemistry has achieved greater importance as a part of chemical science, rather than as an operational appendage of nuclear physics.

The basic principles of radiochemistry have been well worked out on the na turally occuring radioactive elements by such pioneers as Hevesy, Paneth, Fajans, Hahn and others (5). With the extension of radiochemical techniques to all the elements, the field of radiochemistry expanded tremendously as chemists hastened to make use of this powerful new tool for research. The voluminous literature that has been compiled on radiochemical work

necessitates that this discussion be confined to only the
particularly relevant topics of exchange reactions and the
Szilard-Chalmers reaction.

A. Isotopic Exchange Reactions.

Since artificially produced radioactive isotopes have become readily available to scientific workers, a great deal of information concerning the nature of chemical linkages and the mechanism of reactions has been obtained from a study of the exchange of isotopic atoms. The literature of such researches has become quite voluminous and it is not within the realm of this paper to more than mention some general considerations.

The kinetic mechanisms operating in systems at equilibrium or in the steady state can be studied directly by the use of isotopic labeling techniques. In typical experiments on isotopic exchange all participating molecular species are in elementic equilibrium and the overall chemical composition of the system is maintained invariant throughout the experimental period. One or more of the reacting molecules is labelled by incorporation of a radioactive isotope of a constituent atom and observations are made on the rate at which isotopic equilibration is attained.

The rate law for isotopic exchange reactions is first-order in the concentration of isotopic-labelled molecules (15). This generalization is a consequence of the requirement that the overall chemical composition of the reacting system be maintained invariant. Thus, suppose the exchange reaction to be written in the form

$$AX + BX' \rightleftharpoons AX' + BX \tag{1}$$
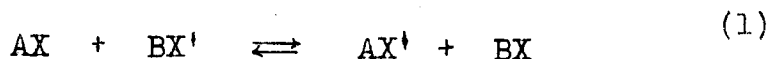
where the prime symbol refers to the isotopically labelled

atom. In such a reaction, there must exist some reversible
mechanism whereby the atomic partners are enabled to exch-
ange positions in the molecules AX and BX. Suppose this
mechanism dictates a rate of exchange R which is any function
of the thermodynamic concentrations and a system variable
such as temperature. Then, the first-order law for the
exchange of isotope is

$$\frac{dx}{dt} = R\left(\frac{y}{b} - \frac{x}{a}\right) \qquad (2)$$

where   a is the concentration in moles per litre of molec-
ules $(AX)+(AX')$, b the concentration of molecules $(BX)+(BX')$, x
the concentration of isotopic molecules (AX') and y, the
concentration of isotopic molecules (BX'). The generalized
equation involving polyatomic types AX_n will be amenable
to the same treatment if the concentration of the reacting
species are expressed in gram atoms per litre. This expr-
ession implies that, no matter what the overall rate of
exchange reaction may be, the rate of appearance of labelled
isotopes in the molecules initially unlabelled follows a
first-order law.

From equation (2) it is easy to show that

$$Rt = -\frac{(a)\,(b)}{(a)+(b)} \ln\left(1 - x/x_\infty\right)$$

where t is the time and x_∞ is the concentration of isotope
in AX at equilibrium.

The requirements for an isotopic exchange then are,
(1)the existence of some reversible equilibrium whereby
the reacting molecular species may consummate the exchange,

and (2) that no isotopic differentiation can occur. It is
important also to note that side reactions due to radiation
effects should be taken care of in control experiments at
different radiation levels.

A great number of experiments have been carried
out by various workers seeking correspondences between types
of chemical bonding and the kinetics of isotopic exchange.
It is of interest to mention some of these experiments here.

The great mass of information gathered about the
structure of molecules using methods based on X-ray diffraction
electron-diffraction, magnetic analysis, measurement of
electric moments, band spectrum analysis, etc., has been
remarkably well correlated and systematized in terms of
the classification of chemica 1 bonds into covalent,electro-
valent and metallic types. Pauling has extended this class-
ification of chemical bond type (17) using a quantum mech-
anical approach based on the additivity of bond energies
calculated from atomic orbital theory.

To evaluate correlations between isotopic exchange
data and bond type, one should neglect systems in which
there exist obvious routes for exchange through ionic mech-
anisms. Systems involving couples such as Br_2 / Br^- , Hg^{++} /
Hg_2^{++}, $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$ etc., have been observed to exhibit
rapid exchange through electron transfer, either through
an ionization mechanism or through an intermediate complex.
However, useful information about such bonds is infrequently
obtained from observations of exchange rates.

Other investigations involve systems for which reaction mechanisms involving bond splitting and dissociation equilibria other than those of ionization are requisite in producing exchange. Bonds between atoms in molecules participating in such exchanges were classified as "pure" covalent or electrovalent or as a mixture of these two extreme types, on the basis of non-isotopic techniques. Then the criterion based on rapidity of exchange was applied to ascertain whether any correspondence existed between degree of covalency and rate of exchange.

In crystalline diphenyliodonium iodide it has been shown by X-ray anlysis (13) that two iodine bonds are covalent and one ionic. The X-ray data are consistuent with a scheme involving the two covalent bonds in the iodonium ion with the ionic bond between the iodonium ion and the iodide viz. $(C_6H_5)_2I^+ - I^-$. When this substance is brought into aqueous solution in the presence of labelled I^- and then recrystallized from solution, labelled iodine is found in the solid. This labelled iodine can be removed with silver ion (as the hydroxide), the resulting $(C_6H_5)_2IOH$ containing no la belled iodine. Furthermore no exchange can be detected between the two iodine atoms of the diphenyliodonium iodide itself (9).

It has been showm by J.F. Flagg, that in cobaltous cobalticyanide, there is no exchange between the cobalt atoms (3). Here the cobaltous atoms are obviously ionic whereas the cobaltic atoms are assumed to be held mainly by covalent bonds by analogy with other cobaltic complexes

for which magnetic susceptibility data are available.

Another experiment illustrating good correlation between covalency and no exchange and between ionic binding and rapid exchange was carried out by F.A.Long in 1941 (11). The research reported on the exchange between free oxalate ions and complex oxalates of iron and cobalt. From measurements of ma gnetic susceptibility it appears that the bonds between the central atom and the oxalate ions in the cobalt complex are covalent whereas in the iron complex they are mainly electrovalent. When these complexes are brought into aqueous solution as the alka li salts in the presence of free oxalate ions labelled with C" it is found that ferric trioxalate exchanges rapidly whereas the cobalt complex shows no exchange.

S. Ruben states that, "many examples may be cited to support the notion that electrovalent linkages lend themselves to rapid exchange and covalent linkages do not. However the cogeny of examples such as those cited is weakened by the fact that in practically all cases the exchange is observed in a polar solvent in which dissociation equilibria operate and what is usually being measured is merely the tendency of ionic linkages to ionize. It is not difficult to find systems in which the readiness of atoms to exchange bears little relation to the assigned bond type". (20).

There is no exchange between magnesium ions and the magnesium porphyrin, chlorophyll, dissolved in an 80% acetone solution. One may assume the central magnesium atom to be held

primarily by electrovalent linkage because of the high degree of electropositive character of magnesium compared to the coordinating nitrogen atoms of the pyrrole constituents of chlorphyll. Nor does exchange occur between Fe^{+++} and ferriheme, ferrihemoglobin, ferric pheophytin and ferric tetraphenylporphin, or between Cu^{++} and cupric pheophytin using various mixed sovents to effect a homogeneous system (20). In ferriheme or ferrihemoglobin, and presumably in the other porphins cited, the magnetic data indicate mainly electrovalent bonding. Yet no exchange occurs.

Another interesting experiment was carried out using the compound ferrous α,α -dipyridyl sulfate $(C_{10}H_8N_2)_3$- $FeSO_4$. The complex salt is known to be diamagnetic and Pauling has concluded that the Fe-N bonds are therefore mainly covalent. Nevertheless an exchange of about 25% with Fe^{++} in aqueous solution was noted after two hours (20).

From a consideration of the data available at present it appears that there need be no systematic correlation between covalency or electrovalency and rate of isotopic exchange. The factors which influence such exchange, i.e. strength of bond, steric hindrance, solvent interactions, equivalent states available, etc., are not yet clearly defined or separable for either extreme type of bonding, let alone for mixed types. Therefore it is permissible only to make the rather attenuated statement that any atom bound in a molecule whether by a covalent or electrovalent bond, will not exchange with similiar atoms in another molecular species unless a mechanism exists for bringing such atoms

reversibly into equivalent states.

It is becoming more apparent to investigators in these researches, that structural relations are very important and perhaps predominate over bond type in determining exchange rate. In the porphin type structures already mentioned it is necessary to break a "fused" ring, i.e. four bonds must be broken simultaneously. Hence one may expect little or no exchange because the "fused" ring structure does not permit the escape of the central atom and the equilibrium involved is practically irreversible in favor of the bound atom. In exchangeable compounds with a ring consisting of separated molecules instead of a "fused" ring type, there exists the possibility of stepwise dissociation with equilibria involving molecular species in which the metal ion is held by two or less bonds.

It has seemed of interest to extend these investigations to another "bound atom" type structure, namely, graphite ferric chloride $(C_{12}FeCl_3)_n$. X-ray studies have shown that the Fe^{+++} ions between the large layer-planes of tightly bonded carbon atoms of the graphite lattice, form a triangular planar network above and below which there is a parallel net plane of Cl^- ions. Rüdorff (22) has found that the magnetic moment of the Fe^{+++} ions in the compound is unchanged with that of Fe^{+++} ions in $FeCl_3$ and suggests that the bonding of the ferric chloride in the lattice is the result of a polarization of the conductivity electrons of the carbon layer-planes toward the central iron ions.

This explanation seems valid, for it would be difficult to account for the extreme inactivity exhibited by graphite ferric chloride if one was to assume that the metallic chloride was held by no more than the van der Waals forces between the lattice layer-planes.

From a consideration of the configuration of atoms around the Fe^{+++} ions in this "sandwich" structure for $(C_{12}FeCl_3)_n$, it seemed unlikely that the iron ions in the compound would exhibit any rapid exchange with Fe^{+++} ions in a queous solution. The series of experiments to be described herein was done to determine whether such exchange took pla ce under any of a variety of conditions.

B. The Szilard-Chalmers Reaction in the Chain Reacting Pile.

A well known field of nuclear chemistry based on the special properties of recoil atoms is that of the Szilard-Chalmers reaction, wherein the radioactive atoms from neutron activation separate themselves from the bulk of material being irradiated (36) (30). The radiative capture of a neutron by a stable nucleus is an important nuclear reaction, which frequently gives rise to a useful radioisotope. However, the chemical identity of the active isotope with the unchanged target element places serious limitations on the specific activities obtained by this reaction. The Szilard-Chalmers reaction, which effects separation of the activated atoms from the target material by virtue of the gamma-ray recoil, can be used to enhance the specific activity of the active material under favorable circumstances.

Three conditions have to be fulfilled to make a Szilard-Chalmers chemical separation possible, (1)The radio-active atom in the process of its formation must be broken loose from its molecule and it must not recombine with the molecular fragment from which it separated. (2) The element must be capable of existence in at least two mutually stable and separable forms. (3) At least two of these forms must show lack of rapid isotopic exchange.

Most chemical bond energies are in the range of 1 to 5 ev. (20-100k. cal. per mole). In any nuclear reaction involving heavy particles either entering or leaving the nucleus with energies in excess of 10 or 100 kev. the kinetic

energy imparted to the residual nucleus far exceeds the magnitude of bond energies. In the case of thermal-neutron capture, where the Szilard-Chalmers method has its most important applications, the incident neutron does not impart nearly enough energy to the nucleus to cause any bond rupture. But neutron capture by a nucleus is accompanied by the release of 8 or 9 m.e.v. of evergy in the form of several energetic gamma quanta. The recoil energy thus imparted to the capturing atom may be as much as one hundred times as great as the energies of the chemical bonds in which it participates. Thus in most n, γ processes the probability of bond rupture is very high.

The third condition for the operation of the Szilard-Chalmers method requires at least that thermal exchange be slow between the radioactive atoms in their new chemical state and the inactive atoms in the target compound. However, the energetic recoil atoms may undergo exchange more readily than atoms with ordinary thermal energies. It is these exchange reactions and other reactions of the high-energy recoil atoms ("hot atoms") that determine to a large extent the separation efficiencies obtainable in Szilard-Chalmers processes (36). Recent attempts to enrich activities produced in the high flux of the chain-reacting pile have shown the high gamma and neutron radiation fields cause marked chemical changes in the bombarded compounds aside from the effects of accompanying activation. That such reactions may yield products similiar to those obtained in activation reactions is to be expected, since both types are essentially a decomp-

osition by excitation. But radiation decomposition can yield small amounts of the chemical form in which the activity is found, thus diluting the active isotope. It is also possible that the radiation field will cause further chemical reactions of the separable active isotope which may change it to a form which is no longer separable, or cause some of the initially separated activity to be lost by a radiation-induced back reaction. As suggested by R.R. Williams, the rate of decomposition is undoubtedly related to different flux components from those responsible for activation (36). Variations among these components must be eliminated or measured before a quantitative test of the proposed rate equations will be possible. Many workers are engaged in a study of these processes and it is likely that much more than the present qualitative data will soon be available.

The reactions which the "hot" atom or fragment will undergo depend to some extent on the nature of its environment and in this connection the present research on the effect of pile irradiation on graphite ferric chloride ($C_{12}FeCl_3$) was carried out.

The largest amount of work in the field of Szilard-Chalmers sepa rations has been done on halogen compounds (29) (32). Many different organic halides (including C_2H_5I, CH_3I, CCl_4, $C_2H_4Cl_2$, C_2H_5Br, $C_2H_2Br_2$, C_6H_5Br) have been irradiated and the products of neutron capture reactions (I^{128}, Cl^{38}, Br^{80}, Br^{82}) removed by various techniques. Se parations of ha logens with 70 to 100 per cent yields have also been

obtained in neutron irradiations of solid or dissolved chlorates, bromates, iodates, perchlorates and periodates.

The bombardment of metal-organic compounds and complex salts is often useful for Szilard-Chalmers separations if the free metal ion does not exchange with the compound and if the two are separable. Some of the compounds which have been used successfully are: cacodylic acid $(CH_3)_2AsOOH$, from which As^{76} can be separated as silver arsenite in 95% yield; copper salicylaldehyde o-phenylene diamine, from which as much as 97% of the Cu^{64} activity can be removed as Cu^{++} ion; uranyl benzoylacetonate, $UO_2(C_6H_5COCHCOCH_3)_2$, from which U^{239} activity has been extracted in about 10% yield. It has been suggested that metal ion complexes which exist in optically active forms and do not racemize rapidly may be generally suitable for Szilard-Chalmers processes because the metal ion in such a complex is not expected to exchange rapidly with free metal ion in solution. Some complexes of this type have been used successfully, e.g. the triethylenediamine nitrates of iridium, platinum, rhodium, and cobalt.

Recent studies of the irradiation of these cobalt complexes have shown the dependence of a successful Szilard-Chalmers' reaction on the configuration of the complexing molecules surrounding the central metallic atom. P. Süe and G. Kayas in 1948, irradiated in a neutron flux, the three cobalticomplexes , hexamine cobalt III nitrate $Co(NH_3)_6$ $(NO_3)_3$, triethylenediamine cobalt III nitrate $Co(en)_3$ $(NO_3)_3$ and diethylenetriamine cobalt III nitrate

Co(tri)$_2$ (NO$_3$)$_3$ (31). They found for all three compounds, that isotopic exchange, within experimental errors, was nil. The percent yields of separated activity, however, varied greatly for the three compounds. From salt no. I, hexamine cobalt III nitrate, they were able to extract 86% of the total activity as the hydroxide. From salt no.II, where the ethylenediamine molecules each take up two positions in the octahedral configuration of the cation, the amount of the activity separated dropped to 75% of the total. In the case of salt no.III, diethylenetriamine cobalt III nitrate, the ethylenetriamine molecules each cover three positions of the octahedral arrangement around the central cobalt atom. Here the Szilard-Chalmers separation was successful to the extent of only 10%.

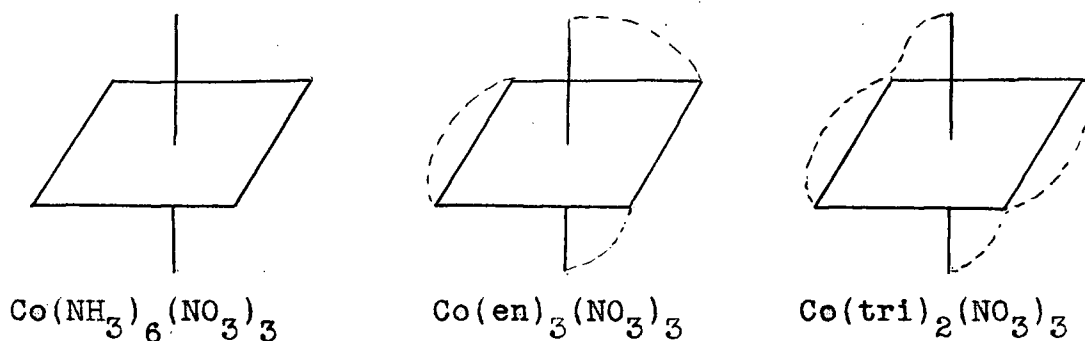Co(NH$_3$)$_6$(NO$_3$)$_3$ Co(en)$_3$(NO$_3$)$_3$ Co(tri)$_2$(NO$_3$)$_3$

Figure 5 - Steric hindrance in cobalt complexes.

These somewhat conclusive results are explained by the authors who state that when an activated recoiling atom of this type is surrounded by a number of large interfering molecules,

that it is more or less improbable that there will follow
any bond rupture allowing the ejection of the "hot" atom
from the compound. It is assumed that, under the effect of
the shock, the coordinating chain enters into vibration and
absorbs sufficient energy to prevent the recoil atom from
leaving the molecule. This steric effect results in the
production of an active compound with most of the A+1 isot-
opic atoms still bonded in the same position as the neutron
capturing atom they replaced.

It is suggested that, in the case of a coplanar mol-
ecule, this steric effect would not be as pronounced, leading
to a fairly high yield of separated activity. It may be of
interest to mention that Szilard-Chalmers reaction on uranium
by means of uranylsalicylaldehyde o-phenylenediimine gives a
yield of about 80% (14). The central atom of this compound
is enclosed in a large and coherent organic molecule and the
high yield is likely due to the probable coplanarity of the
molecule which enables the uranium atom to escape.

Consider now the case of the very stable graphite ferr-
ic chloride $(C_{12}FeCl_3)_n$ with the ferric chloride molecules
bound between the layer-planes of carbon atoms in the graphite
lattice. As has been suggested, the probability of any rapid
isotopic exchange between ferric ions in solution and the
iron existing as ferric chloride bound in the graphite lattice,
seems somewhat remote. It is therefore likely that any iron
activity separated by a Szilard-Chalmers process on this
compound could be obtained in high specific activity.

However the configuration of atoms surrounding each iron atom in this "sandwich" structure, would very definitely be expected to contribute to a large retention of the activity by recombination reactions, and result in a low yield of separated activity following neutron irradiation.

The success of a Szilard-Chalmers separation on $(C_{12}FeCl_3)_n$ was determined following irradiation of a dry purified sample of the compound in Canada's National Research Council atomic pile. The results and discussion of these experiments follow in the experimental section of this paper.

3. RADIOCHEMICAL TECHNIQUES.

In radioactive tracer experiments, a radioactive
isotope is used as an indicator to trace or follow the path
taken by the inactive isotope. The radioactive isotope decays
with the emission of alpha, beta, or gamma rays, or possibly
positrons and these radiations can be measured with a suitable
instrument such as an ionization chamber or a Geiger counter.
By taking suitable precautions, the measurements can be made
quantitative.

The decay of a radioactive substance follows the
exponential law
$$N = N_0 e^{-\lambda t}$$
where N is the number of unchanged atoms at time t, No is
the number present at $t = 0$, and λ is the decay constant. The
half-life $t_{\frac{1}{2}}$ of a radioactive species is given by

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$$

In practical work the number of atoms N is not
directly evaluated, a nd even the rate of change dN/dt is
usually not measured absolutely. The usual procedure is to
determine the activity A, with $A = c\lambda N$. The detection coeff-
icient C, depends upon the nature and efficiency of the
recording instrument and the geometrical arrangement of sample
and detector. In cases where the decay of the radioactive
species is appreciable during the course of the experiment
it is necessary to correct for the resulting decrease in act-
ivity before comparative determinations can be obtained.

The limit of sensitivity of a Geiger-Müller counter
is set by the background counting rate which must be subtrac-

ted to find the activity of the sample. By sheathing the enclosed counter with a few centimeters thickness of lead most of the ionization from small amounts of activity present as impurities in construction materials, and from the appreciable and variable amount of radon, thoron, and their decay products contained in the air, can be eliminated. However the cosmic-ray effect will still be significant and results in a background counting rate of from 20-25 counts per minute.

Because radioactive decay is a random process, ultimate accuracy in assay of radioactivity is limited by statistical fluctuations inherent in counting data. This random phenomenon is subject to established methods of statistical analysis which have been verified abundantly by experiment. The term "standard deviation" as used in the experimental section of this thesis is equal to the square root of the number of counts observed. The probable error, defined as the error which is as likely to be exceeded as not, is 0.6745 times the standard deviation. In general, the counting is sufficient in duration to make the standard deviation less than errors from non-statistical sources such as sampling uncertainties and uncontrollable chemical losses.

In the research to be described, only relative counts from activities were required and many of the corrections necessary to obtain an absolute count, such as external absorption loss, backscattering and sample geometry, were eliminated by standardization of counting techniques. A complete description of the experimental methods followed in

this research has been included in the experimental section
of the thesis. It has seemed more convenient to leave any
discussion concerning the validity of counting rate results
and the justification of the manner of handling the required
correction problems until that more appropriate time.

EXPERIMENTAL.

1. **Preparation of Graphite Ferric Chloride,** $\left[C_{12}FeCl_3\right]_n$.

In view of the nature of the experiments to be carried out, it was decided that the fully intercalated graphite ferric chloride $\left[C_{12}FeCl_3\right]_n$ would be better suited to our purpose than the second compound containing less ferric chloride. Accordingly, it was the compound containing about 56% ferric chloride which was prepared in all cases by keeping the reaction temperature below 309°C.

a.) **Anhydrous Ferric Chloride:** Dry Cl_2 was passed over C.P. iron powder contained in an electrically heated Pyrex tube at 350°C. Beautiful hexagonal platelets of a deep red wine color formed throughout the cool portion of the tube. Dry air was admitted during the cooling and the crystals were removed and handled only in a dry box. To prepare the active chloride, radioactive iron wire was used together with the powder.

b.) $\underline{C_{12}FeCl_3}$: Acid purified, 200 mesh graphite, (G-66 Graphite powder-FisherScientific Co.) was mixed with three times its weight of anhydrous ferric chloride, sealed in a Carius bomb tube, and heated for twelve hours at 305°C. The approximately 47% of the reaction product which is excess ferric chloride was removed by successive refluxings with hot 6N HCl. After a total washing time of 36 hours a further refluxing at 100°C with a one gram sample gave no test for Fe^{+++} with NH_4CNS or less than 4.3μgm. Fe as determined radiometrically. 6N NaOH at 80°C showed no action on the

graphite ferric chloride after purification. The compound
was stable in air and decomposed at temperatures only above
309°C (with evolution of $FeCl_3$ vapour).

From the initial weight of graphite and final weight
of compound, the percentage composition was determined and
found always to correspond to $C_{12}FeCl_3$, a compound containing
53% ferric chloride. According to Rüdorff (22) this same
composition results throughout the preparation range 200 to
309°C. and independently of the original graphite crystal
form (8).

X-ray diffraction measurements on the $C_{12}FeCl_3$ powder,
made with a Phillips-Geiger Counter X-ray Spectrometer and
using the 1.539 Å Cu line, showed three peaks at d=9.40,
4.66 and 3.13 Å . The first of these has been interpreted
by Rüdorff as the separation of the planes of carbon atoms.
His value was 9.4 Å .

In the three tables which follow, are set down the
numerical results from X-ray diffraction measurements on
graphite, anhydrous ferric chloride and $C_{12}FeCl_3$. In the
column headed "degrees" is listed the glancing angle, equal
to twice the θ in the Bragg equation $n\lambda = 2d \sin\theta$. The
second column contains the values of d, the distances between
reflecting atomic planes. The values I/I_0 listed in the third
column, are the ratios of the intensity of the reflected beam
of X-rays to the greatest intensity observed. The values
listed for anhydrous ferric chloride in Table II. have been
obtained from the literature. Tables I and III contain the

values obtained for graphite and $C_{12}FeCl_3$ from diffraction measurements made in the laboratories of the British Columbia Research Council, who so kindly permitted the use of their X-ray Spectrometer.

TABLE I

X-ray Diffraction Measurements on Graphite

Graphite   3.36   1.68   2.02

Degrees (2θ)	dÅ	I/I₀	
24.0	3.701	0.13	
26.5	3.36	1.0	*
41.2	2.187	0.1	
42.2	2.137	0.13	
43.0	2.100	0.16	
44.8	2.02	0.3	*
46.0	1.969	0.12	
50.2	1.82	0.1	
54.5	1.68	0.7	*
56.2	1.63	0.09	
60.0	1.539	0.1	
61.6	1.503	0.06	
77.0	1.236	0.21	
83.7	1.154	0.19	
85.0	1.139	0.06	
86.4	1.122	0.13	

TABLE II

X-ray Diffraction Measurements on Anhydrous Ferric Chloride.[x]

| $FeCl_3$ | 2.68 | 2.08 | 5.9 |

Degrees (2θ)	d$\overset{\circ}{A}$	I/I_o	
15.0	5.90	0.32	*
17.4	5.10	0.05	
18.5	4.79	0.06	
19.8	4.50	0.03	
29.4	3.03	0.03	
33.4	2.68	1.00	*
37.4	2.40	0.02	
43.5	2.08	0.40	*
46.2	1.96	0.03	
52.1	1.75	0.30	
55.0	1.67	0.06	
56.5	1.63	0.16	
63.5	1.46	0.06	
70.1	1.34	0.05	
80.5	1.19	0.03	
87.2	1.12	0.05	

x A.S.T.M.Philadelphia,Pa.,X-ray diffraction powder patterns
J.D.Hanawalt and co-workers,card index.

TABLE III

X-ray Diffraction Measurements on Graphite Ferric Chloride $C_{12}FeCl_3$.

$C_{12}FeCl_3$	9.4	4.66	3.13	
Degrees (2θ)	d$\overset{\circ}{A}$		I/I_0	
8.1	10.90		0.30	
9.4	9.40		0.64	✳
11.8	7.49		0.25	
19.0	4.66		1.00	✳
26.8	3.32		0.21	
28.5	3.126		0.81	✳
35.5	2.524		0.09	
45.9	1.973		0.07	
52.2	1.42		0.11	
55.1	1.663		0.09	
58.8	1.567		0.10	
63.6	1.464		0.08	
68.1	1.374		0.12	
80.2	1.195		0.05	
80.8	1.187		0.05	
81.8	1.175		0.09	

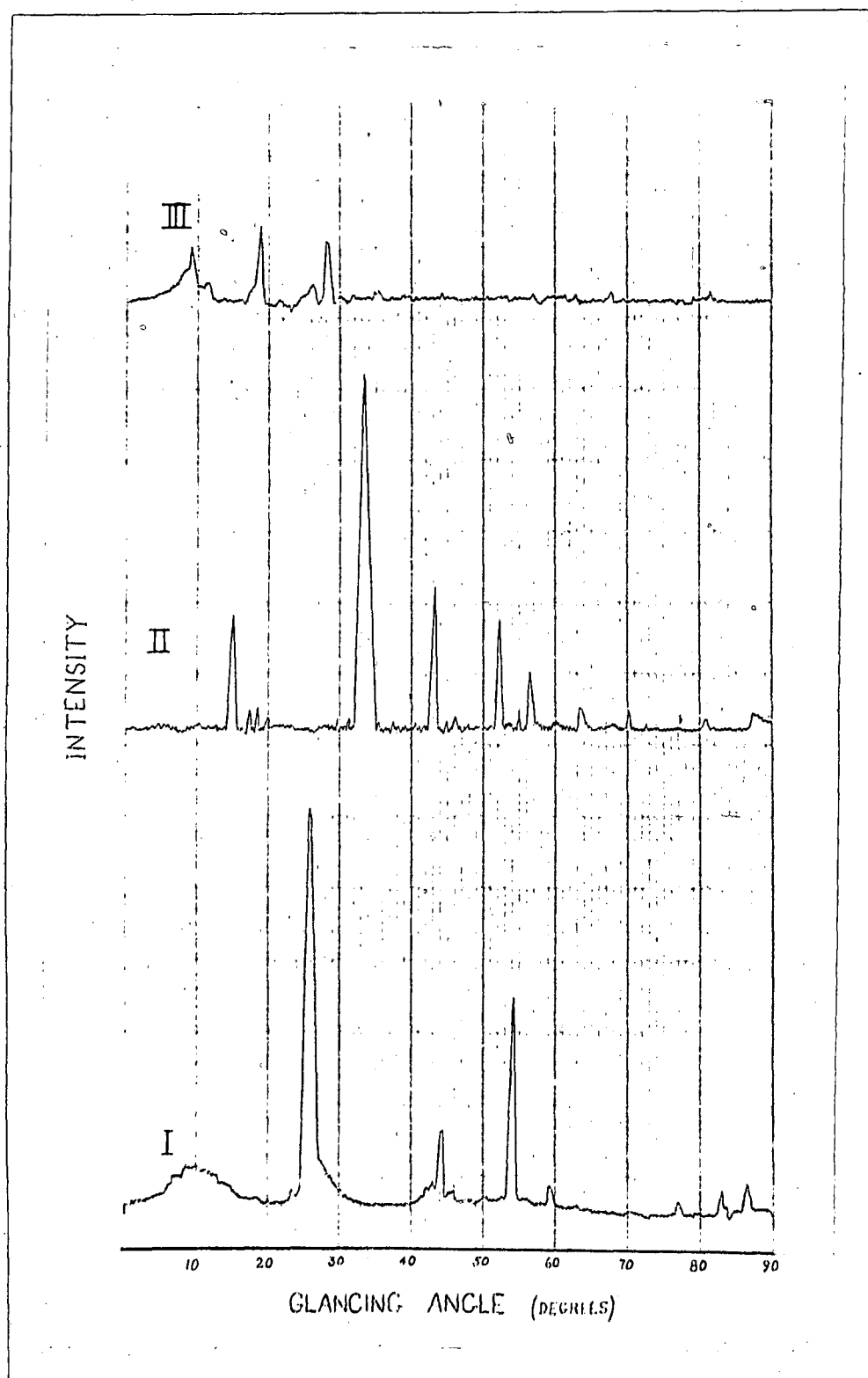Plate I : X-Ray diffraction patterns of

    I - Graphite
    II - Anhydrous Ferric Chloride
    III - Graphite Ferric Chloride.

Plate I shows the comparison between the three X-ray diffraction diagrams. I - graphite, II - anhydrous ferric chloride and III - graphite ferric chloride ($C_{12}FeCl_3$). It will be seen that the pattern for graphite ferric chloride is distinctly different from that of either graphite or ferric chloride a nd it is apparent that no free ferric chloride exists in the compound.

The value obtained for the percentage ferric chloride in the compound compares very well with the limiting value of $FeCl_3$:C equal to 1:12.04 required by the crystal structure as determined by Rüdorff. Rigorously purified specimens gave the consistent figure 53% ferric chloride, which corresponds to a $FeCl_3$:C ratio of 1:12.02. This figure which is somewhat better than the value 1:11.9 reported by Rüdorff (22) is probably due to the longer period of acid-leach purification employed in this work.

In view of the experiments to follow, it was necessary to determine to what degree of certainty the last traces of free ferric chloride had been removed from the purified $C_{12}FeCl_3$.

1). 5 gms. of $C_{12}FeCl_3$ were purified by successive refluxings in 6N. HCl for thirty-six hours. This specimen was then treated to a further refluxing in 100mls. of 6N. HCl for six hours, and the acid extract tested for Fe^{+++} with 1% NH_4CNS solution. The NH_4CNS reaction with Fe^{+++} which is well adapted to spot tests has a sensitivity of 0.25 μ.g.m. Fe^{+++} and a concentration limit of 1 in 200,000.

The acid extract solution was evaporated to 10 mls. before testing. 1 ml. portions gave no coloration with the reagent and were therefore assumed to contain less than 5 μ. gm. Fe^{+++}. Therefore the 100 ml. acid extract from the 5 gm. sample of $C_{12}FeCl_3$ could not have contained more than 50 μ. gm. Fe^{+++}, or less than 10 μ.gm. Fe^{+++} per gram of graphite ferric chloride tested.

2). A second test for completeness of removal of free Fe^{+++} was made using radioactive $C_{12}FeCl_3$. The active $C_{12}Fe^{*}Cl_3$ was measured at 229×10^3 counts per minute per gm. which was equivalent to 229×10^3 c.p.m. from 0.1820 gm. Fe . The sample was treated by the 36 hour washing procedure and then examined as follows:

5 gms. $C_{12}Fe^{*}Cl_3$ refluxed with 100mls. 6N HCl for 4 hours.

The 100ml. acid solution was evaporated to 10ml. and tested for activity.

1ml. acid extract soln. gave 440 ± 21 counts/10 min. $=44\pm2$ c.p.m.

Background count = 44 ± 2 c.p.m.

Probable error $0.6745\times 2 = \pm1.35$ c.p.m.

Maximum activity due to Fe^{+++} in extract = 2×1.35 c.p.m./ml. = 2.7×10 c.p.m. in total volume of extract.

229×10^3 c.p.m. are recorded from 0.1820 gm. Fe.

$\therefore$ Max, Fe in acid extract $= \dfrac{27}{229\times10^3} \times 0.1820 = 21.5$ μ.gm. from 5 gm. $(C_{12}FeCl_3)$

$\therefore$ less than 4.3 μ.gm. Fe extractable/gm. $C_{12}FeCl_3$

From a consideration of the above results it appeared reasonably certain that we were dealing with $C_{12}FeCl_3$, and of sufficient purity to be suitable for use in the following experiments on exchange and the Szilard-Chalmers reaction.

2. Tests for Exchange between Graphite Ferric Chloride $C_{12}FeCl_3$ and Ferric ion, using Radioactive Fe^{59}.

The exchange experiments were performed by shaking portions of finely powdered radio-active graphite iron (59) III chloride in solutions of inactive ferric ion of various P.H.'s, temperatures, and solvents. The reverse procedure, using radioactive iron (59)III chloride solutions, was also carried out in some cases. These mixtures were mechanically shaken for various lengths of time, then separated by centrifuging. Aliquots were withdrawn and the specific activity of the active components determined from the counting rate, corrected for decay.

The conditions of the experiments were varied considerably but the same general procedure was followed in every case. Tests for exchange were carried out in acid media. As well as ferric chloride, aqueous solutions of ferric nitrate and ferric sulfate were mixed with the active compound. To test the effect of temperature on the rate of exchange all the mixtures in aqueous media were shaken at temperatures of both 20 and 80° C. The influence of solvent interaction on the exchange was observed by carrying out experiments using ferric chloride dissolved in ethanol, diethyl ether, iso-propyl ether, acetone and benzyl alcohol. In one experiment using benzyl alcohol as the media, tests for exchange between graphite ferric chloride and ferric ions were made at a temperature of 190° C.

<u>Radioactivity Measurements</u>:   Pure iron wire was activated in the neutron flux of the Canadian N.R.C. pile at Chalk River, Ontario.   A mixture of the 47 day Fe^{59} emitting 0.26 and 0.46 Mev. beta's and 1.10 and 1.30 Mev. gamma's and the 4 year Fe^{55} which decays by K capture emitting 0.07 Mev X-rays, was received with an activity of 0.059 mc. Fe^{59}/gm. plus about 0.29 mc. Fe^{55}/gm.   This was mixed with Fe powder and converted to ferric chloride as already described.

The decay curve (Fig. VI), over a five month period is linear with a $T\frac{1}{2}$ of 47 days, indicating no need for a correction for the weak Fe^{55} radiation.

Measurements were made with an "end on" G.M. self quenching counter made by the U.B.C. Physics Department. It had a $3mg./cm^2$ window 2.0cm. in diameter, and a 150 volt plateau which was flat within 1% statistical error and over which the count increased 8%. (Fig. VII) The counter was mounted on a lucite base and shielded to a background count of 42 ± 2 counts per minute.   The pulses were counted by a Nuclear Instrument Co. Model 163 scaling unit.   Response was linear to 2% up to 3300 counts/minute.

Samples were counted on 1" diameter watch glasses, placed in an easily reproducible position about 3cm. below the counter window.   The samples of graphite ferric chloride compared were always less than 0.2 mg. per $cm.^2$ and hence no self absorption correction was made in calculating specific activity.   The initial activity was 0.1 µc. per gm. of compound, corrected only for background.   The evaporated ferric chloride solution samples however, were often thick
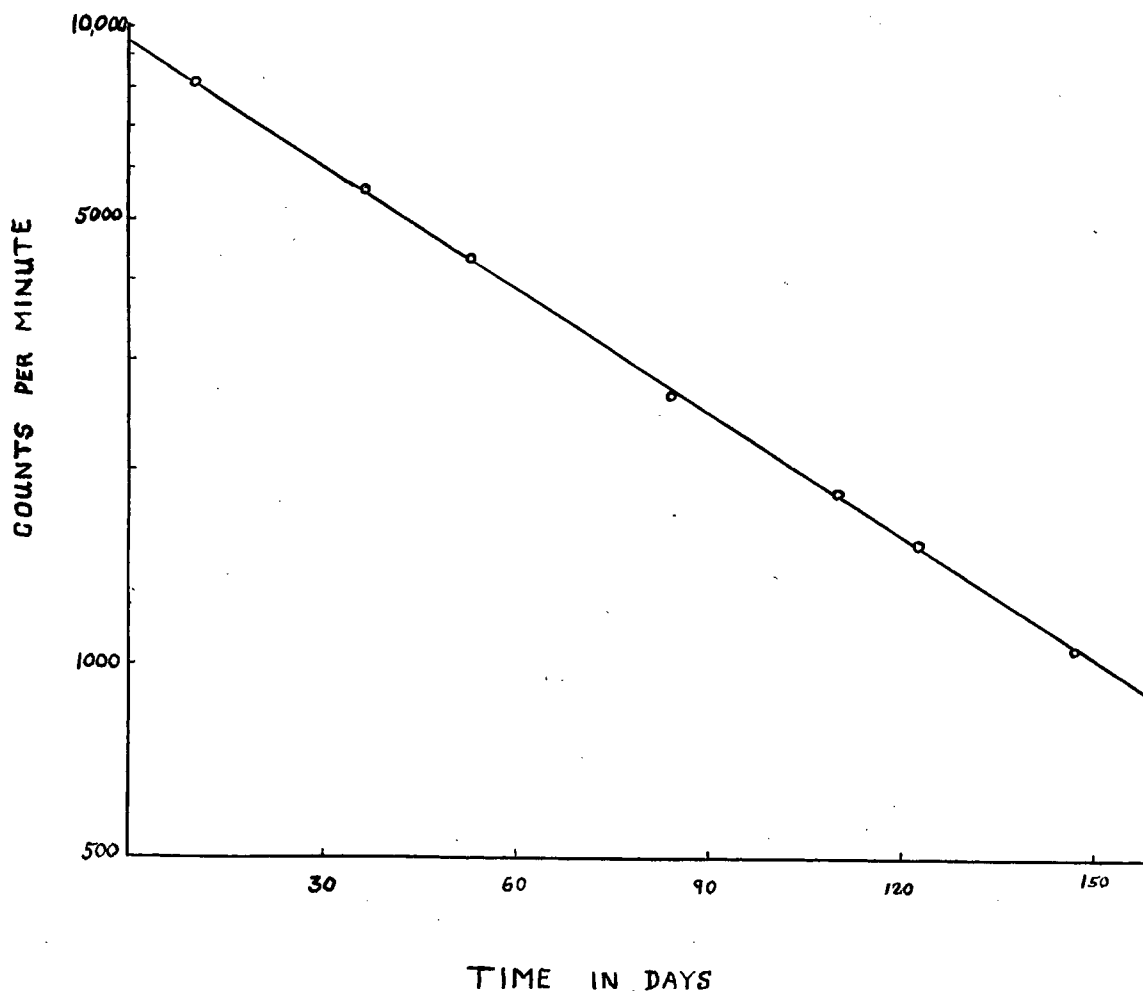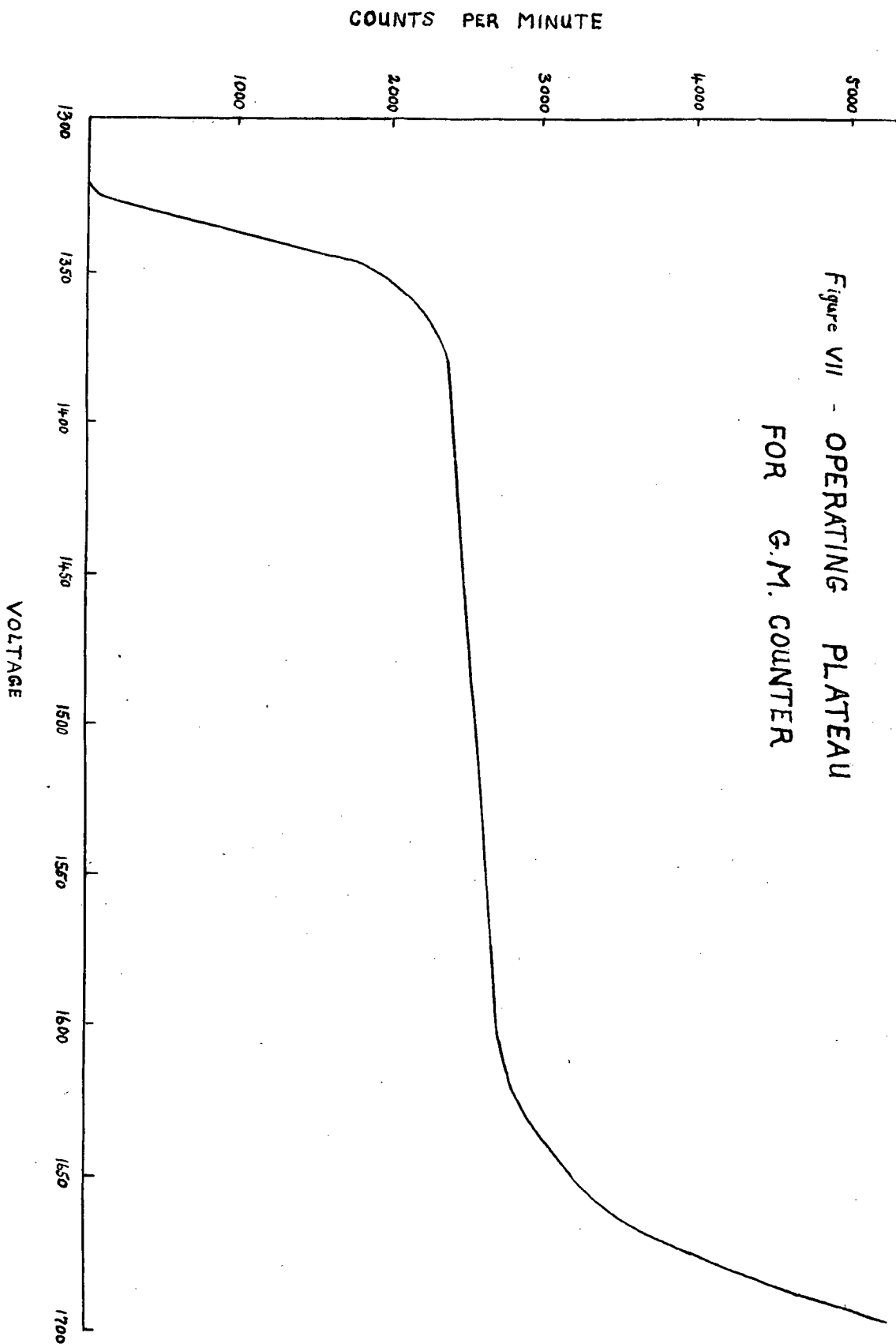
Figure VI - Rate of decay of radioactive Fe^{59} .

COUNTS PER MINUTE

Figure VII - OPERATING PLATEAU
FOR G.M. COUNTER

VOLTAGE

enough to require a self absorption correction. This was handled in the usual fashion. Aliquots of 0.2, 0.4, 0.6 and 0.8 ml. of solution were pipetted onto the watch glasses, evaporated to dryness using an infra red lamp, and counted. The measured activity per unit volume of sample in each case was calculated (apparent specific activity), and plotted against the actual volume of the sample used. From this curve, extrapolated to zero volume (i.e. zero thickness of sample) was obtained the true specific activity. The solutions of radioactive iron (59) III chloride used were prepared from a standard 0.4M solution of P.H. 1.0. The activity of this solution corrected as above and for background was 580 counts per minute per mg. of iron. Later measurements of both solid and solution were corrected for decay back to this time.

Exchange Measurements: A 0.01 to 0.15 gm. sample of $C_{12}FeCl_3$ was mechanically shaken with 5ml. of a solution containing ferric ion and centrifuged. The specific activity of the washed solid and of the solution were determined (and corrected for background and decay, and in the case of the evaporated solution aliquot, for self absorption) as described above.

The variations made in the conditions were:

1) P.H. : 0.2 to 3.0

2) Temperature : 20 to $80°C$. for water and to $190°$ for benzyl alcohol.

3) Solvent for $FeCl_3$: water, ethanol, acetone, diethyl ether, isopropyl ether, benzyl alcohol.

4) Anion : chloride, nitrate, sulfate.

5) Active iron in the compound only or in the solution only.

6) Time of shaking.

7) Concentration of ferric ion and weight of compound.

RESULTS AND DISCUSSION.

The data obtained on the exchange of graphite ferric chloride and ferric ions in acid solution, are presented in Table I. The quantity I/c represents the specific activity expressed in arbitrary units. I is the counting rate in counts per minute corrected for decay, and C is the number of milligrams of iron present in the sample of the graphite ferric chloride being counted. In column 7 is recorded the specific activity of the original graphite iron (59) III chloride, in column 8 its specific activity after remaining for the recorded length of time in the solution described, and in the last column the specific activity calculated for complete exchange.

The results of the experiments reported in Table I show that no appreciable exchange takes place between $C_{12}Fe^{*}-Cl_3$ and Fe^{+++} in acid solution within periods of time up to twelve hours. Further observations on some of these reaction mixtures were made after they had been shaken for ninety-six hours, and again after standing in the laboratory for a period of four months. In all cases the exchange was negligible. (Table II).

Reaction temperatures above room temperature were obtained by connecting a hot water circulatory system to the mechanical shaker. Where tests for exchange were made using an aqueous medium a maximum temperature of 80° was used. Table III shows the results obtained from comparisons at different temperatures, of tests for exchange

Tests for Exchange between $C_{12}Fe^*Cl_3$ and Fe^{+++} in Aqueous Acid Solution at $20 \pm 2^\circ$ C.

No.	$C_{12}Fe^*Cl_3$ gms.	$FeCl_3$ soln. mls.	Conc. of $FeCl_3$ M.	P.H.	Time of Shaking	I/C (original)	I/C (obs. at time t)	I/C (∞ calc.)
1.	0.025	5	0.01	1.1	4 min.	1259±9	1257±8	780
2.	0.025	5	0.01	1.1	2 hrs.	1259±9	1251±10	780
3.	0.010	5	0.05	3.0	1 hr.	1260±10	1249±14	145
4.	0.010	5	0.05	3.0	8 hrs.	1260±10	1249±12	145
5.	0.025	5	0.10	1.2	4 min.	1260±10	1253±14	176
6.	0.025	5	0.10	1.2	2 hrs.	1260±10	1262±10	176
7.	0.030	5	0.167	1.0	4 min.	1257±11	1254±10	131
8.	0.030	5	0.167	1.0	6 hrs.	1257±11	1251±11	131
9.	0.025	5	0.25	1.0	4 min.	1255±8	1261±10	78
10.	0.025	5	0.25	1.0	12 hrs.	1255±8	1260±9	78
11.	0.025	5	0.10	2.5	8 hrs.	1257±11	1259±10	176
12.	0.050	5	0.5	0.5	1 hr.	1250±10	1254±10	78
13.	0.050	5	0.5	0.5	4 hrs.	1250±10	1246±10	78
14.	0.100	5	0.78	0.2	4 min.	1258±8	1252±10	100
15.	0.100	5	0.78	0.2	4 hr.	1258±8	1254±10	100
16.	0.100	5	0.78	0.2	10 hrs.	1258±8	1246±12	100
17.	0.150	5	1.0	0.5	4 min.	1252±10	1260±10	123
18.	0.150	5	1.0	0.5	8 hrs.	1252±10	1248±10	123

TABLE I

(50)

No.	Composition	P.H.	I/C (original)	I/C (after 4min. shaking)	I/C (after 96hrs. shaking)	I/C (after 4mo. contact)	I/C (∞calc.)
1.	0.01gm. $C_{12}Fe^*Cl_3$, 5ml. 0.05M $FeCl_3$.	3.0	1260±10	1262±10	1248±10	1252±10	145
2.	0.025gm. $C_{12}Fe^*Cl_3$ 5ml. 0.1M $FeCl_3$.	1.2	1260±9	1253±14	1255±10	1259±10	176
3.	0.025gm. $C_{12}Fe^*Cl_3$ 5ml. 0.25M $FeCl_3$.	1.0	1255±8	1261±10	1260±10	1248±10	78
4.	0.05gm. $C_{12}Fe^*Cl_3$ 5ml. 0.5M $FeCl_3$.	0.5	1250±10	1259±10	1251±10	1242±10	78
5.	0.10gm. $C_{12}Fe^*Cl_3$ 5ml. 0.780M $FeCl_3$.	0.2	1258±8	1252±10	1239±10	1247±10	100
6.	0.15gm. $C_{12}Fe^*Cl_3$ 5ml. 1.0M $FeCl_3$.	0.5	1252±10	1260±10	1247±10	1245±10	123

Tests for Exchange between $C_{12}Fe^*Cl_3$ and Fe^{+++} in Acid

Solution at $20 \pm 2°C$.

After 4 minutes, 96 hours and 4 months.

TABLE II

TABLE III

Effect of Temperature on Tests for Exchange between $C_{12}\overset{*}{Fe}Cl_3$ and Fe^{+++} in Various Acid Solutions.

No.	$C_{12}\overset{*}{Fe}Cl_3$ (gms.)	Conc. 0.05M (5mls.)	Media of Exchange	Temp. (°C.)	Time	I/C (original)	I/C (at time t)	I/C (∞calc.)
1.	0.010	$FeCl_3$	H_2O	20	96hr.	1260±10	1254±10	145
2.	0.010	"	"	80	8 hr.	1257±10	1245±10	145
3.	0.010	$Fe(NO_3)_3$	"	20	96hr.	1259±12	1240±10	145
4.	0.010	"	"	80	8 hr.	1255±12	1250±10	145
5.	0.020	$Fe_2(SO_4)_3$	"	20	96hr.	1268±10	1255±10	145
6.	0.020	"	"	80	8 hr.	1256±10	1250±10	145
7.	0.010	$FeCl_3$	EtOH	20	96hr.	1257±10	1258±10	145
8.	0.010	"	"	50	4 hr.	1262±12	1264±10	145
9.	0.010	$Fe(NO_3)_3$	"	20	96hr.	1262±12	1252±10	145
10.	0.010	"	"	50	4 hr.	1251±12	1245±10	145
11.	0.020	$Fe_2SO_4)_3$	"	20	96hr.	1253±10	1248±10	145
12.	0.020	"	"	50	4 hr.	1257±10	1247±10	145
13.	0.010	$FeCl_3$	Acetone	20	96hr.	1249±10	1252±10	145
14.	0.010	"	Diethyl ether	20	96hr.	1257±10	1241±10	145
15.	0.010	"	Isopropyl ether	20	96hr.	1251±10	1255±10	145
16.	0.010	"	Benzyl alcohol	20	96hr.	1257±10	1250±10	145
17.	0.010	"	"	80	4 hr.	1254±10	1257±10	145
18.	0.010	"	"	190	4hrs.	1258±12	1242±10	145

between graphite ferric chloride and ferric iron in solutions of water, ethyl alcohol, acetone, diethyl ether, isopropyl ether and benzyl alcohol. The influence of both solvent interaction and temperature appear to be nil. Even at a temperature of about 190° C with boiling benzyl alcohol no exchange was observed after four hours refluxing.

To complete the rather strong evidence that no exchange takes place between $C_{12}FeCl_3$ and Fe^{+++}, one further set of experiments was performed. In the experiments set forth in tables I, II and III, radioactive graphite iron (59) III chloride was brought into contact with inactive ferric iron in solution and after suitable periods of time the components were separated and their specific activity ascertained. In no instance was any appreciable activity detected in the inactive iron containing species nor was there any transfer of activity from the solid compound.

In the above experiments however, no account was taken of the possibility of preferential adsorption of the migrating active ions by the active compound. If exchanging active ions, trapped in the complex by capillary condensation were not removed by washing the compound before counting, there would of course be no decrease in the specific activity of the solid. Likewise no increase in the activity of the ferric ion solution would be observed. Therefore tests for exchange between radioactive iron (59) III chloride and inactive graphite ferric chloride were carried out. The results of these experiments are shown in table IV.

No.	$\overset{*}{FeCl_3}$ 5 mls. (M.)	PH	$C_{12}FeCl_3$ (gms.)	I/c (original)	I/c (after 4hrs.)	I/c (after 96hrs.)	I/c (after 4mo.)	I/c (∞ calc.)
1.	0.4	1.0	0.150	582±6	584±6	580±6	570±6	468
2.	0.25	1.0	0.150	580±5	581±5	584±5	578±5	417
3.	0.10	1.0	0.150	581±6	580±6	587±6	585±6	292
4.	0.08	1.0	0.150	584±6	575±6	578±6	570±6	262
5.	0.06	1.0	0.150	582±6	580±6	582±6	576±6	220
6.	0.04	1.0	0.150	580±6	572±5	572±5	569±6	170
7.	0.01	1.0	0.150	579±6	575±6	579±6	574±6	54
8.	0.005	1.0	0.150	580±6	581±6	580±6	578±6	28

Tests for Exchange Between $\overset{*}{Fe}^{+++}$ and $C_{12}FeCl_3$ in Aqueous Acid

Solution at $20 \pm 2^{\circ}C$.

TABLE IV.

As before, no measureable exchange was observed even after long periods of time. The samples of inactive graphite ferric chloride were easily washed clear of any activity following separation from the radioactive ferric chloride solution.

3. The Szilard Chalmers Reaction with Graphite Ferric Chloride.

It has been shown that there is no measurable exchange between $C_{12}Fe\,Cl_3$ and ferric ion in surrounding solution. It is therefore likely that any iron activity separated by a Szilard-Chalmers process on the compound could be obtained in high specific activity. It is of interest to note the success of a Szilard-Chalmers separation, with regard to the structure of this compound.

Pure $C_{12}FeCl_3$ was irradiated in the neutron flux of the Canadian N.R.C. pile at Chalk River, Ontario. The activity of the compound was measured, the separated portion of activity removed in hot hydrochloric acid solution, and the yield calculated.

1.50gms. of $C_{12}Fe\,Cl_3$ powder (containing 0.27gm. Fe) were activated by 48 hours irradiation at about 3.9 10^{12} n./cm.^{2}/sec. A mixture of the 47 day Fe^{59} and 4 year Fe^{55} was obtained, but as well, the reactions occuring on neutron irradiation of chlorine resulted in the production of four other active isotopes. Cl^{35} undergoes an (n,γ) reaction to produce the 10^6 year Cl^{36} emitting 0.66 Mev. beta's, an (n,p) reaction producing 87 day S^{35} which emits 0.17 Mev. beta's, and also an (n,α) reaction to 14.7 day P^{32} emitting 1.7 Mev. beta's. Cl^{37} also undergoes an (n,γ) reaction to Cl^{38} which has a 37 minute half life and decays with the emission of 1.1, 2.8 and 5.0 Mev. beta's and 1.65 and 2.15 Mev. gamma's.

Because of its long half life, the Cl^{36} radioactivity developed is negligible when relatively short irradiation periods are used. Short-lived Cl^{38} decays in a day or so. Contamination by P^{32} is of the order of 1% of the total S^{35}, in terms of beta particles emitted (35). The initial activity of the irradiated compound was estimated at 0.008 mc. Fe^{59}/gm., 0.027 mc. Fe^{55}/gm. and 1.27 mc. S^{35}/gm. The separated portion of the activity from the Szilard-Chalmers reaction would then be expected to be composed mainly of these three radioactive isotopes. The iron activities can be separated by a very efficient and simple S^{35} extraction procedure based on the solvent extraction of ferric chloride (34). In the experiments reported here, diethyl ether was used as solvent. The partition coefficient for extraction of ferric chloride by diethyl ether from aqueous 6N hydr- chloric acid is about 100.

0.100 gm. of pile irradiated graphite ferric chloride was refluxed with constant boiling ($\sim$6N) hydrochloric acid for six hours and the aqueous solution separated by centrif- uging. A few drops of 30% hydrogen peroxide were added, to ensure that all the iron was present as ferric ion. The colorless aqueous solution was shaken with successive 1/4 volumes of diethyl ether saturated with hydrochloric acid, and finally washed with an equall volume of solvent. The ether extracts were then collectively stripped with distilled water. The radioactivity of the resultant solutions was mea- sured and the components differentiated by adsorption meas-

urements.

Figures VIII, IX and X give the absorption curves for the aqueous residue solution, the stripped ether, and the water extract respectively. It is evident that no detectable amount of radioactive iron remains in the aqueous residue, nor can the activity of S^{35} be detected in the extract. Apparently the P^{32} is present in a form which has a small but measurable partition coefficient, as it is extractable to some extent. The small amount of S^{35} taken up by the solvent (possibly as sulfur chloride) is not re-extracted by distilled water. The chemical form of the S^{35} in the aqueous residue is presumably as $Fe_2(S^{35}O_4)_3$. In a similiar type of solvent extraction of irradiated $FeCl_3$, M.B. Wild (35) has reported 99.5% of the original S^{35} and 83% of the P^{32} to be contained in the aqueous residue solution which is free of detectable Fe^{59}. The stripped ether portion contained only the remaining 0.5% of the S^{35} and 0.01% of the P^{32}. All the original Fe^{59} and the small amount of remaining P^{32} was found in the water extract which was free of detectable S^{35} activity.

The total activity of the hydrochloric acid solution, which had been refluxed for six hours with the 0.100 gm. sample of irradiated $C_{12}FeCl_3$, was measured at 0.682% of the activity of the untreated compound. No detectable activity was obtained in a further treatment with hot HCl solution.

The very low energy of the beta particles from S^{35}

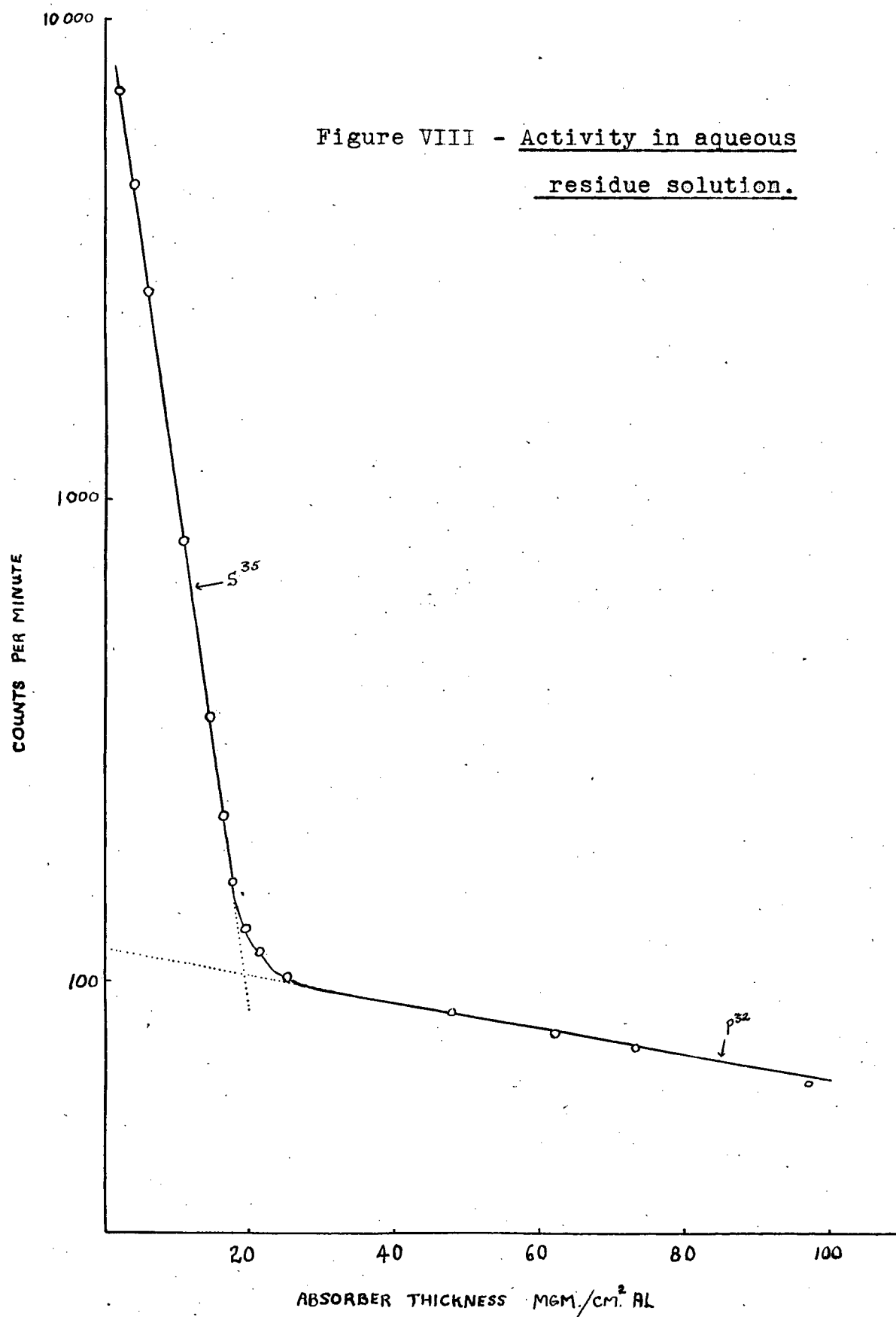Figure VIII - Activity in aqueous residue solution.

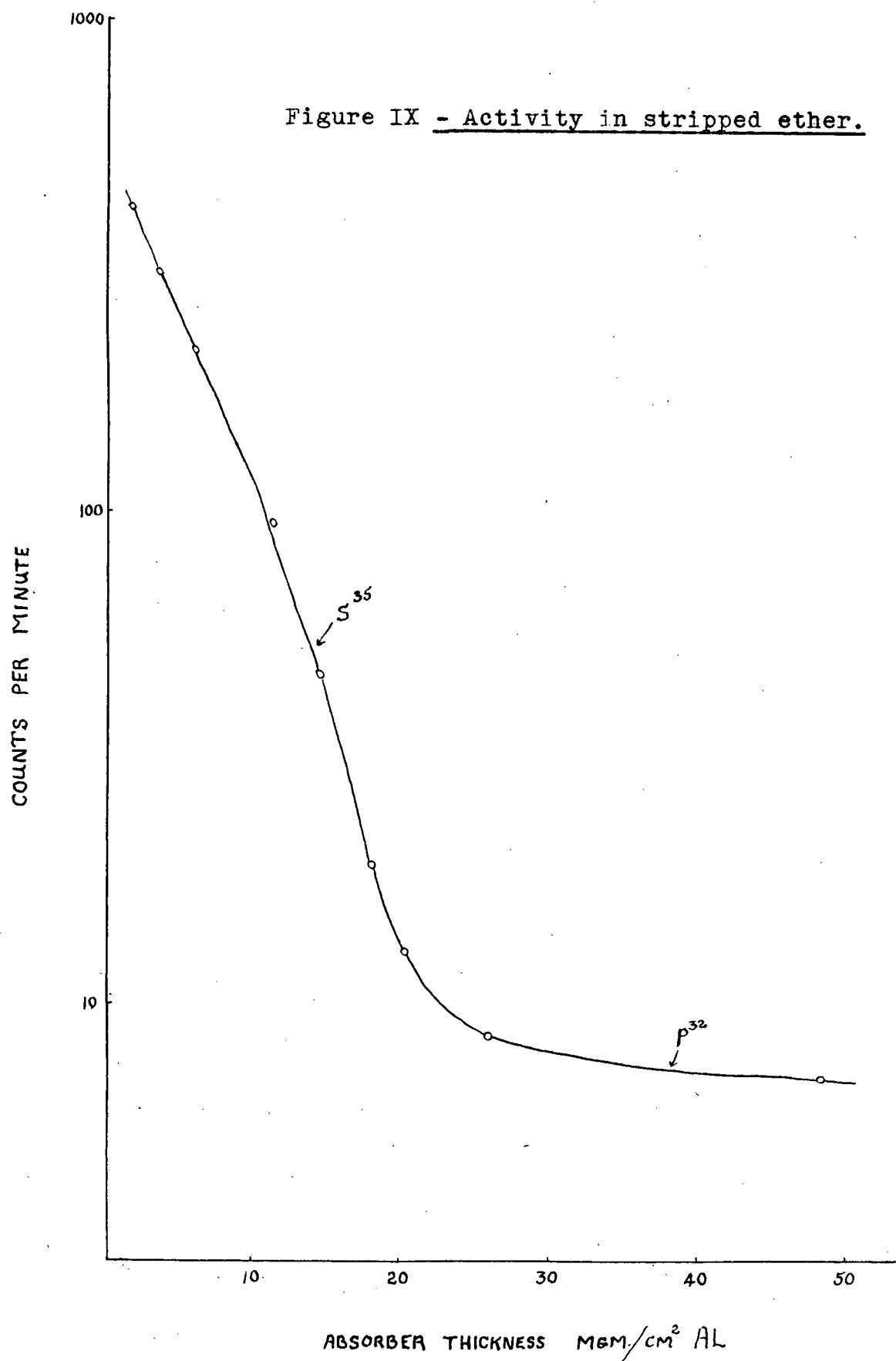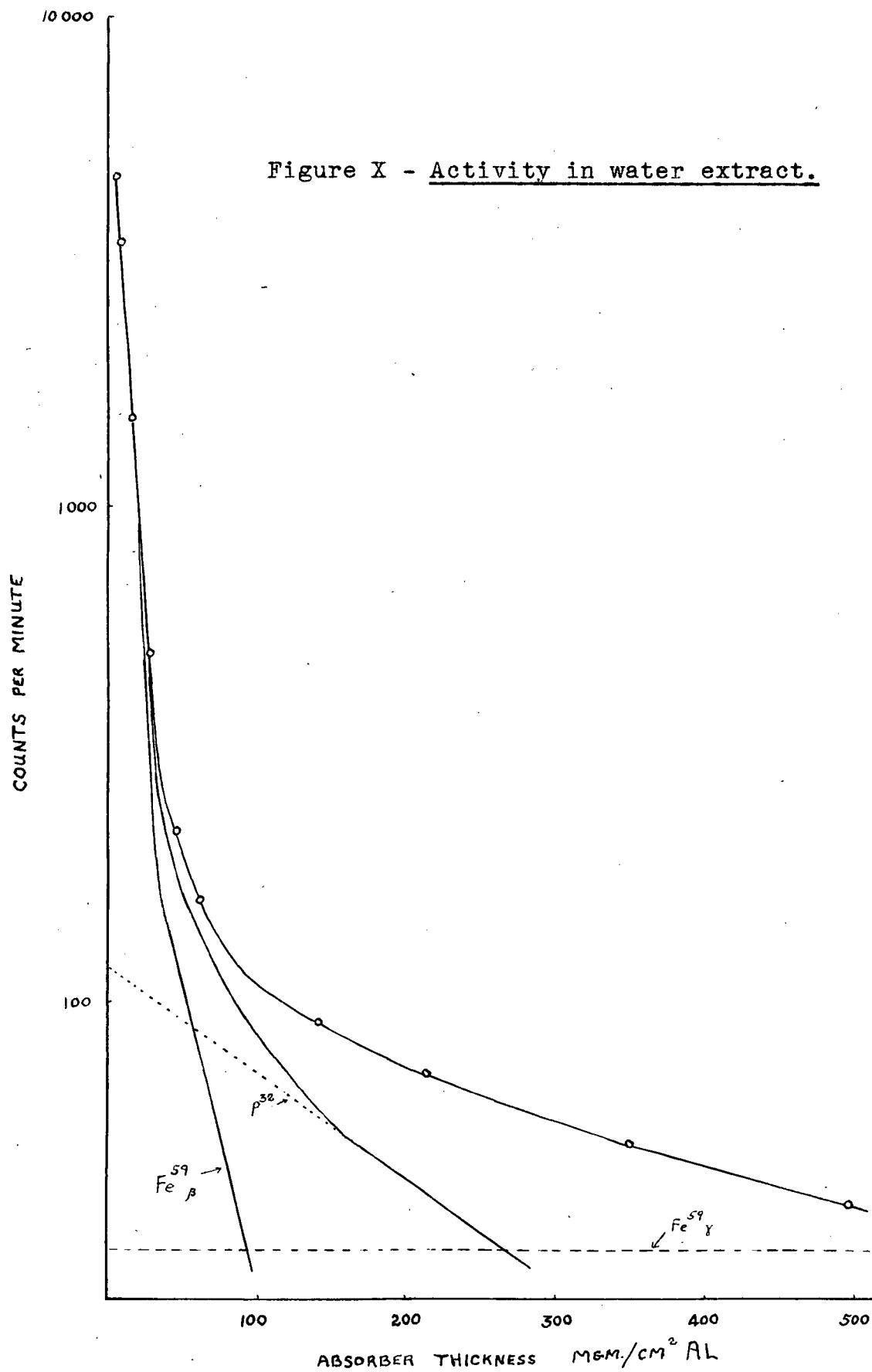Figure IX - Activity in stripped ether.

Figure X - Activity in water extract.

poses special problems as regards their quantitative detect-
ion. The low energy of the radiation makes the self-weaken-
ing effect a major one. Experiments have shown that samples
of thickness 3 mgm./cm^2 will be weakened to the extent of
40% of the total activity (35). In activity measurements
of the various solutions involved, the self absorption
corrections were obtained in the same manner as already
discussed under exchange experiments. The graphite ferric
chloride samples compared were always less than 0.2 mgm./cm^2.

The activity of the irradiated $C_{12}FeCl_3$ was compared
with the activity of hydrochloric acid solution containing
the separated isotopes, by absorption measurements on the
two. Both samples measured were less than 0.2 mgm./cm^2.
Figure XI gives the absorption curves comparing I - irrad-
iated $C_{12}FeCl_3$ and II - evaporated acid extract solution.
It will be seen that the two absorption curves are ident-
ical. From this it seems apparent that the component radio-
active isotopes exist in the activity separated by the
Szilard Chalmers reaction in the same ratio as they are
present in the irradiated compound. A third series of
absorption measurments on the irradiated compound from which
the separated portion of activity had been removed gave a
curve identical with the other two.

It is apparent that some of the recoiling atoms of
both chlorine and iron have achieved bond rupture and
ejection from the $C_{12}FeCl_3$ lattice. However, the very low
fraction of the total activity separated in hot hydrochloric

Figure XI – Comparison of activities of
          irradiated $C_{12}FeCl_3$ and
          separated activity, following
          Szilard-Chalmers reaction.

1) Irradiated $C_{12}FeCl_3$
2) Separated activity.
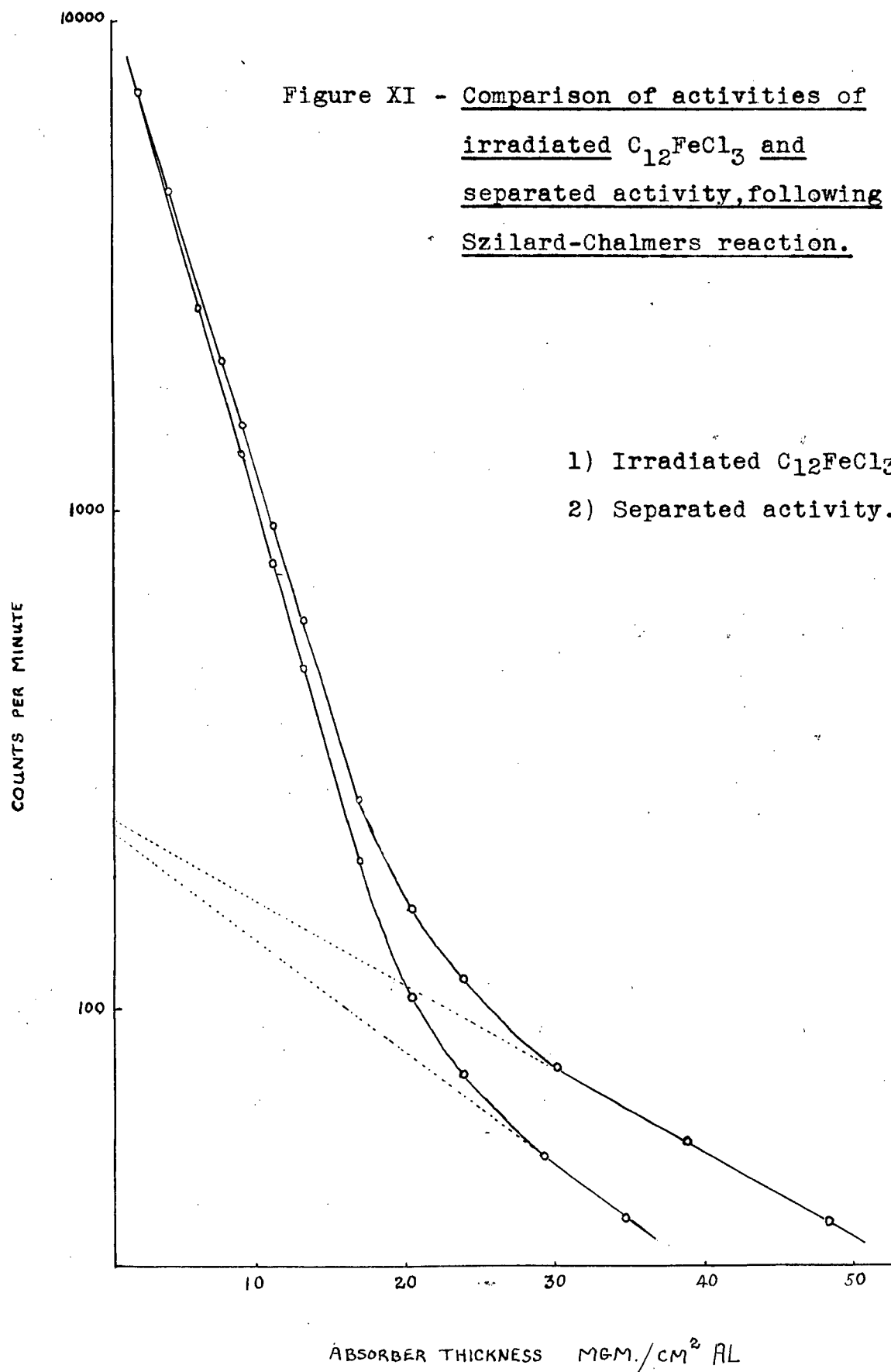
acid, indicates that almost all the neutron capturing atoms are still firmly bound in the graphite compound. A series of experiments, designed to see whether or not changing the method of recovering the separated activity would result in a larger Szilard-Chalmers yield, was carried out. Samples of the irradiated compound that were refluxed with ~6N HCl for four, eight and sixteen hours, relinquished no more of their total activity than did a sample which was washed for 15 minutes in a solution of 4N HCl at 80° C. The values for the percentage of total activity separated, which were obtained from these experiments, were all within the range 0.681 to 0.688%. It was noted, however, that if the irradiated graphite ferric chloride was subjected to a fine grinding previous to the acid-leach treatment, the fraction of activity separated increased slightly. The percentage yield was raised from about 0.684% to an average value of 0.727% by grinding the samples by hand in a mortar or between ground-glass plates. The use of a fine aluminum oxide grinding powder raised this value to 0.737%. The results from these above experiments are listed in Table V.

In all cases the aqueous acid solutions containing the separated activity, were colorless and gave no test for Fe^{+++} with NH_4CNS. It is therefore apparent that little or no radiation decomposition takes place as a result of the irradiation of the compound. It is unfortunate that the small amount of iron separated is not detectable by other than radiochemical methods, as facilities for handling the large

TABLE V.

The Effect of Different Extraction Methods on

the % Szilard Chalmers Separation.

Exp. No.	Conditions for acid extraction of separable activity from $C_{12}FeCl_3$.	Initial activity of $C_{12}FeCl_3$ (c.p.m.)	Separated activity in HCl soln. (c.p.m.)	%Szilard Chalmers separation.
1.	0.0827gm. in 4N HCl at 80°C. Stirred in blender for 15 min.	58.11×10^5	39.6×10^3	0.681
2.	0.200gm. in ~6NHCl at 100°C. Refluxed for 4 hours.	134.32×10^5	92.4×10^3	0.688
3.	0.200gm. in ~6N HCl at 100°C. Refluxed for 8 hours.	120×10^5	82×10^3	0.683
4.	0.1523gm. in ~6N HCl at 100°C. Refluxed for 16 hours.	87.06×10^5	59.4×10^3	0.682
5.	0.1094gm. in ~6N HCl at 25°C. Ground in a mortar(approx. 1 hr.)	38.56×10^5	28.08×10^3	0.728
6.	0.0482gm. in ~6N HCl at 100°C. Sample ground between two ground-glass plates before acid extraction.	11.99×10^5	8.7×10^3	0.7255
7.	0.0530gm. in ~6N HCl at 100°C. Sample ground as in #6, but with fine Al_2O_3 grinding powder.	13.187×10^5	9.72×10^3	0.737

activities that would be necessary to make a quantitative determination of the specific activities of iron and sulfur, were not available.

DISCUSSION of RESULTS.

It has been shown that the Szilard-Chalmers separation on $C_{12}FeCl_3$ is successful to less than 1%. As has been already suggested, this result does not appear too surprising when one considers the structure of the compound under discussion. Above and below the planar ferric ion network there is a parallel triangular net plane of chloride ions, and above and below these planes of chloride ions there is a tightly bonded hexagonal plane of carbon atoms. This arrangement repeated through the lattice, serves to produce formidable steric hindrance effects for an atom of either iron or chlorine which might leave the lattice. This has been shown in tests for exchange between the Fe^{+++} ions bound in the graphite lattice and Fe^{+++} ions in surrounding solution. No measurable exchange was observed even after a four month period.

The retention by the $C_{12}FeCl_3$, of over 99% of the activity developed by neutron irradiation may possibly also be explained by the pronounced steric effect. Recombination of "hot" fragments (in a so-called reaction cage) would appear to be quite probable in a solid material of this type. The separation of activity which does result from the Szilard-Chalmers reaction (approx. 0.68%), cannot be explained on the basis of impurities in the $C_{12}FeCl_3$. It has been shown that the purified compound contained less than 4 μ.gm. Fe/gm. as free ferric chloride. This amount could only account for 0.3% of the fraction of activity that was separated, even if it were all extractable following irradiation.

One theory which might explain the small separation of activity, is that it is only the edge atoms in this "stacked layers" structure which are able to break away following neutron capture. This idea finds some support in the experiments which showed that grinding the powdered compound to a finer size increased to some extent the fraction of activity separated. Thus the percentage yield was raised from 0.684 to 0.737% presumably due to the breaking of the crystals and exposure of new edges from which irradiation freed active atoms were removed by the hydrochloric acid solution.

It would be of interest to subject samples of $C_{12}FeCl_3$ of different particle size to neutron irradiation and compare the Szilard-Chalmers yield. Also there is the possibility that the irradiation of the compound for a shorter period or in a lower neutron flux might lead to a more successful separation of activity. Radiation experiments have shown that the establishment of a successful Szilard-Chalmers enrichment reaction in experiments of low flux or short bombardment, does not ensure its success when longer or more intense bombardments are employed. It may be that in the case of $C_{12}FeCl_3$, some of the initially separated activity is lost by a radiation - induced back reaction. This situation does not seem too likely, since the separable form represents a less complicated breakdown product of the starting material. The Szilard-Chalmers enrichment experiments with antimony pentafluoride (R.R. Williams (36)) however, show this loss of activity

without apparent decomposition. The activity in the separable form dropped from 60 to 5% of the total after several hours bombardment at constant pile power. Nevertheless, it seems apparent that even under more suitable conditions, a compound of the graphite ferric chloride type could not be expected to give any appreciable separation of activity by a Szilard-Chalmers reaction.

SUGGESTIONS for FURTHER RESEARCH.

1. It is probable that graphite ferric chloride and the other graphite compounds described represent only a few of the"stacked layer" structures which are capable of existance. Rüdorff has attempted the preparation of graphite compounds of AsI_3, SbI_3, BiI_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, $AlCl_3$, $CoCl_3$ and $CrCl_3$, without result. (22) There is little doubt however, that further research will bring to light additional examples of molecules penetrating between the layer planes of the graphite lattice to form more or less stable structures.

2. The idea that it is only a few exposed edge atoms that are able to achieve bond rupture and subsequent ejection from the crystal lattice of $C_{12}FeCl_3$, could be investigated. The neutron irradiation of samples of different particle size (different ratio of edge atoms to total atoms) might possibly lead to greater percentage yields of separated activity.

3. A further research concerning a study of radiation effects on graphite ferric chloride would be of interest. The correlation between flux intensity and period of bombardment and fraction of activity separable, could be ascertained.

BIBLIOGRAPHY.

(1)   Bernal, J.D.,   Proc. Roy. Soc.   Acvi   749   (1924)

(2)   Bragg, W.L.,   Proc. Roy. Soc.   A89   277   (1913)

(3)   Flagg, J.F.,   J. Am. Chem. Soc.   63   577   (1941)

(4)   Fredenhagen, Cadenbach, and Suck,
            Z. anorg. allg. Chem.
                                    158   249   (1926)
                                    178   353   (1929)

(5)   Hevesy, G., and Paneth, F., Manual of Radioactivity,
            Oxford University Press, (1938)

      Hahn, O., Applied Radiochemistry,
            Cornell University Press, (1936)

(6)   Hofman, U.,   Naturwissenshaften,   32   260   (1944)

(7)   Hofman, U., and Frenzel, A.,   Z. Elektrochem.,
                                    40   511   (1934)

(8)   Hull, A.W.,   Phy. Rev.,   X   661   (1917)

(9)   Juliusberger, F., Topley, B., and Weiss, J.,
            J. Chem. Soc.,   p.1295   (1935)

(10) Laidler, D.S., and Taylor, A.,   Nature,
                                    146   130   (1940)

(11) Long, F.A.,   J.Am. Chem. Soc.,   63   1353   (1941)

(12) Manguin, C., Bull. Soc. Franc. Min.,
                                    XLIX   32   (1926)

(13) Medlin, W.V.,   J. Am. Chem. Soc.,   57   1026   (1935)

(14) Melander, L.,   Acta Chem. Scand.,   1   169   (1947)

(15) McKay, H.A.C.,   Nature,   142   997   (1938)

(16) Ott, H., Ann. Physik.,   LXXXV(IV) 81   (1928)

(17) Pauling, L.,   The Nature of the Chemical Bond
            Cornell University Press, 2nd Edition,
                                    (1948)

(18) Riley, H.L.,   Journ. Inst. Fuel,   X   149   (1937)

(19) Riley, H.L.,   Fuel   24   8   (1945)

(20) Ruben, S., Kamen, M.D., Allen, M.B., and Nahinsky, P.
                 J. Am. Chem. Soc.,   64   2297 (1942)

(21) Rüdorff, W.,   Z. anorg. Chem.   245   383   (1941)

(22) Rüdorff, W.,   Field Information Agency, Technical(F.I.A.T)
                 Review of German Science   1939-46
                 Inorganic chemistry,   Part I   239   (1948)

(23) Rüdorff, W. and Hofmann, H.,
                 Z. anorg. Chem.,   238   1   (1938)

(24) Rüdorff, W., and Rüdorff, G.,
                 Chem. Ber.,   80   413   (1947)

(25) Rüdorff, W., and Schulz, H.,
                 Z. anorg. Chem.,   245   121   (1940)

(26) Ruess, G.L.,   Monatsheften,   76   381   (1947)

(27) Ruff, O., and Brettschneider, O.,
                 Z. anorg. Chem.,   217   1   (1934)

(28) Schleede and Wellman,
                 Z. Physik, Chem.   XVIII   1   (1932)

(29) Seaborg, G.T.,   Chem. Rev.,   27   199 (1940)

(30) Steigman, J.,   Phy. Rev.,   59   498 (1941)

(31) Süe, P., and Kayas, G.,
                 Jour. Chem. Phys.,   45   188 (1948)

(32) Szilard, L., and Chalmers, T.A.,
                 Nature,   134   462   (1934)

(33) Thiele, H.,   Kolloid-Z.,   56   129 (1931)

(34) Welcher, F.S., Organic Analytical Reagents,Vol.1   (1947)

(35) Wilk, M.B., Canadian Journal of Research,
                                         27   475 (1949)

(36) Williams, R.R., J. Phy. Coll. Chem., 52   603 (1948)