THE γ-RAY INDUCED OXIDATION OF Fe^{+2} ION IN DILUTE AQUEOUS SOLUTION

by

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INTRODUCTION

In 1895, Roentgen (1) discovered that invisible rays emanating from an electrical discharge tube produced blackening of a covered photographic plate. In the following year Becqueral (2) observed a similar phenomenon produced by invisible rays from uranium-containing compounds. These were the first observations of a chemical change produced by ionizing radiations. The discovery of the radioactivity of radium by Mme. Curie (3) in 1898 led to the observation of a multitude of other effects produced by these radiations. For example, it was a matter of great concern that aqueous solutions of radium compounds continuously evolved hydrogen and oxygen. In the following years many researches were undertaken in an effort to understand the mechanism by which these ionizing radiations produced chemical changes. By 1921 so many data had accumulated that Professor Lind published his monograph entitled "The Chemical Effects of Alpha Particles and Electrons" (4). This was later revised and a second edition published in 1928. In 1938, Eyring, Hirschfelder and Taylor (5) gave a quantitative theoretical interpretation of chemical reactions produced in the gas phase by ionizing radiations.

Prior to the outbreak of World War II experimental work in radiation chemistry was confined to the use of very low intensity sources. Only the most wealthy laboratories could afford even a gram of radium and most research workers had to be content with millicurie amounts of radium and low voltage X-ray equipment. Thus, as a rule, irradiation times were very long and in some cases extended over several months before any detectable changes were observed.

With the birth of the Manhattan Project during the early years of World War II, more powerful sources of radiations became available for study of the chemical and physical effects produced by high energy radiations. At that time, the prime concern was to determine or predict, on the basis of existing knowledge, the effects of intense irradiation on the construction materials that were to be used in the building of a high energy pile. For the first time the powerful machines of the nuclear physicist, such as cyclotrons and Van de Graaff generators, were applied to radiation chemical studies. Thus, intensities several thousand times greater than those used prior to 1940 became available for studies in this field.

Interaction of Radiations with Matter

The high energy radiations which are used in radiation chemical studies are all characterized by their ability to ionize the absorbing medium and are commonly called ionizing radiations. These radiations may be classified as follows:

a) light particles: X- and γ-rays, β-particles, cathode rays
b) heavy particles: α-particles, protons, deuterons, neutrons.

The absorption of energy from radiations in the light particles group is attributed to the production of fast secondary electrons. For

X- or γ-rays, the energy absorption may take place by the photoelectric effect, by the Compton (scattering) effect or by pair formation. For long wave-length X-rays ($\lambda > 0.1$ Å), the mechanism of energy absorption is primarily by the photoelectric effect. The energy of a quantum is completely absorbed and results in the ejection of an electron (photoelectron). The photoelectron has all the energy of the original quantum less its binding energy in the atom. This energy ultimately appears as a long wave-length X-ray or as an Auger electron. Therefore, the entire energy of the original quantum has been absorbed. For shorter wave-lengths ($\lambda \leqq 0.1$ Å), part of the absorption is by the photoelectric effect, but a second mechanism, the Compton effect, is becoming more important. In this process, the energy of the original quantum is partitioned between the recoil electron and the scattered quantum, the partition of energy being determined by the angle of scatter. The scattered quantum can also be absorbed by the medium. The third mechanism of energy absorption involves pair formation. This is important for wave-lengths < 0.01 Å. In this process, the quantum is completely converted into an electron and a positron. The positron is quickly destroyed with another electron giving rise to a γ-ray quantum, so called 'annihilation radiation', which can be absorbed by one of the two previous mechanisms.

The relative importance of the three processes of energy absorption depends largely upon the energy of the quantum and the atomic number of the absorbing element. Regardless of the mechanism of energy absorption the net effect will be the production of fast secondary electrons. The projection of fast secondary electrons in matter involves the transfer of energy. Electrons lose energy in traversing matter because a rapidly moving charged particle exerts electrical forces on the electrons of atoms and molecules near which they pass, causing electronic excitation or ionization. The secondary electrons also make elastic collisions with atoms, but because of their small mass, practically no energy is thus transferred. It has been found experimentally that as the velocity of the secondary electron decreases the amount of ionization increases to a maximum. The net result of the absorption of energy from X- or γ-radiation will be an almost uniform distribution of ions throughout the irradiated zone (6).

The interaction of an alpha particle with matter will be discussed as a typical example of the heavy particle group. An alpha particle produces a very large number of ions along its path, the number of ions produced per unit length of path (specific ionization) being a function of the velocity of the particle. Ionization results mainly from elastic impacts with the electrons of the absorbing material. Because the mass of an alpha particle is much greater than the mass of an electron, the energy loss in a single collision is only a small fraction of the total kinetic energy, consequently a large number of collisions is necessary to stop an alpha particle. Energy may also be lost by elastic collisions with the nuclei of the absorbing atom. The energy loss of an alpha particle is accompanied by ionization. The amount of energy used in producing an ion pair is much greater than the ionization potential of the material. This is due partly to the fact that the electrons possess a certain kinetic energy after being separated from the atom, and partly to processes of excitation which do not contribute to the ionization. With this type of radiation there is produced dense columnar ionization with primary absorption concentrated in the axis of the column and absorption due to the secondary electrons occurring at the edges of the column (6).

The absorption of energy from heavy particles is fundamentally different from that for light particles. This is due to the fact that an X-ray quantum disappears in a single elementary absorption process (exponential absorption), whereas, for alpha particles, the absorption is due essentially to elastic impacts with the electrons of the absorbing medium.

RADIATION CHEMISTRY OF WATER AND AQUEOUS SOLUTIONS

(A) WATER

The decomposition of water by high energy radiations is one of the oldest and most studied reactions in radiation chemistry. Giesel (7) was the first to observe the evolution of gas from water containing radium bromide. Bodländer (8) analyzed this gaseous mixture and found it to contain 12% oxygen and 88% hydrogen, the excess of hydrogen being 64%. In their experiments Ramsay and Soddy (9) found the gas mixture to contain 29.8% oxygen and 70.2% hydrogen, the hydrogen excess being 10.8%. They attributed this excess of hydrogen to oxidation of the stopcock grease by the radiation. In 1907, Ramsay (10) re-investigated this phenomenon, being careful to eliminate all sources of error and concluded that the proportion of hydrogen gas is always greater than in electrolytic gas.

Between 1907 and 1908 Cameron and Ramsay (11) published a series of papers on the chemical action of radium emanation on water. They found that the mixture of hydrogen and oxygen gas initially contained an excess of hydrogen. By extracting the irradiated water with pure freshly distilled ether they were able to demonstrate the formation of hydrogen peroxide by the yellow colour which formed when titatium sulfate was added to the ether extract. In 1909, Kernbaum (12) reported on the decomposition of water by the penetrating radiation of radium. He observed that initially the gases evolved contained a large excess of hydrogen and that hydrogen peroxide was formed in amount equivalent to the oxygen deficiency in the gas mixture. The gradual decrease in hydrogen excess he attributed to the decomposition of the hydrogen peroxide.

In 1910, Bergwitz (13), using a polonium source furnished by Giesel, studied the decomposition of water by alpha particles with the polonium source deposited on copper foil. Since hydrogen peroxide was not observed, Bergwitz assumed that the oxygen deficiency might have been due to oxidation of the copper plate on which the polonium was deposited. From a consideration of his data LeBlanc (14) noted the similarity between the alpha ray effect and the requirements of Faraday's law.

Lind (15) in 1912 discussed the apparent equivalence between the chemical effects produced by alpha rays in gases and the amount of ionization in the gas. He also considered the relation between the chemical effects produced by alpha rays in liquids and the total amount of ionization, with the added assumption that the total ionization for a given substance is independent of its state of aggregation. From an analysis of the existing literature (work of Debierne (16), Cameron and Ramsay (11) abd Usher (17)) he was able to show a striking equivalence between the number of molecules reacting and the number of ions formed, utilizing the number of ions formed had the liquid existed as a gas. Lind concluded that the ionic yield, M/N, where M is the number of molecules decomposed and N is the number of ion pairs formed, for alpha rays was generally unity, and suggested that ions are probably the primary initiator of the reaction.

In the following year, Duane and Scheuer (18), working in the laboratory of Mme. Curie, studied the decomposition of water in the three states of aggregation by alpha particles. Their radiation source was simply a thin walled capillary glass tube containing radon which was immersed in the liquid water. With this arrangement the amount of energy absorbed was easily determined by measuring the saturation ion current in an air chamber. They found the rate of gas evolution to coincide with the rate of decay of radon if the volume of gas liberated was corrected by adding an amount of oxygen equivalent to the excess of hydrogen. The ionic yield (M/N) was found to be 0.87. They concluded that water is decomposed in a primary reaction as follows,

$$H_2O \longrightarrow H_2 + O$$

and that hydrogen peroxide results from a secondary reaction of nascent oxygen on water,

$$H_2O + O \longrightarrow H_2O_2.$$

In addition, they found that ice at -180°C evolved hydrogen and oxygen under the action of alpha rays, but that the ionic yield (M/N) was considerably less than in the liquid state. The hydrogen and oxygen were always evolved in electrolytic proportions from which Duane and Scheuer concluded that at this temperature ice is not acted on by nascent oxygen. The extremely low ionic yield (M/N) obtained for water vapour was attributed to the recombination of products (hydrogen and oxygen) under alpha irradiation.

In contrast with the alpha ray decomposition of pure water, O. Risse (19) announced in 1929 that pure air-free water does not decompose under the action of X-rays. This inability of X-rays to decompose pure air-free water was confirmed by Fricke and Brownscombe

(20) in 1933, with more accurate methods of analysis. Hydrogen and oxygen were determined with a van Slyke apparatus, and hydrogen peroxide by electrometric titration; both methods were reported to be sensitive to about one micromole per liter. With dosages up to 150 kiloroentgens hydrogen peroxide and oxygen were not found. However, small quantities of carbon dixoide and hydrogen were found but were ascribed to organic impurities, because the amount of gas obtained was independent of dose above a few kiloroentgens. They concluded that pure air-free water is not decomposed by X-rays. In later experiments, Fricke (21) took extreme precautions to free the water of organic impurities. The water, as vapour, mixed with washed oxygen, was passed through a quartz tube heated to 900°C. With this method he was able to reduce considerably the organic impurities in the water, but they were not completely removed. This was shown by the production of hydrogen and carbon dioxide when this carefully purified water was irradiated with X-rays. Fricke concluded that the best way to purify water was to irradiate it with X-rays. However, he found that even water purified in this way always gave one or two micromoles per liter of hydrogen gas, and he stated that "we could not be sure whether oxygen or hydrogen peroxide were also produced".

Nurnberger (22) in 1934, working in the laboratory of Professor Lind, investigated the alpha ray decomposition of water as a possible method for determining the transmission of alpha ray bulbs. He described two methods, called the direct and indirect, of irradiating liquids with alpha rays from radon. In the former, radon was mixed directly with the liquid, whereas in the latter radon was confined to a small alpha ray bulb situated in the liquid. In his work, Nurnberger emphasized the necessity of using absolutely clean apparatus, for he wrote that "impurities in the liquid chamber may inhibit or accelerate the action of alpha rays and therefore should be eliminated". In agreement with earlier work, he observed that the production of gas was proportional to the quantity of radon and that the large initial excess of hydrogen decreases as the reaction proceeds. In general, the results obtained with the indirect method exhibited departures from the results with the direct method. In this connection it is noteworthy that with the alpha ray bulbs only about 8% of the alpha ray energy was transmitted to the water, consequently the effects of the beta and gamma rays would be considerably enhanced. From a consideration of (i) gaseous product lost by absorption in the water, (ii) gaseous product lost by recombination in the gas phase (under action of alpha rays), and (iii) partition of radon between liquid and gas phase, he calculated an ionic yield (M/N) of 0.78.

In 1936 Nurnberger (23) demonstrated the production of hydrogen peroxide in alpha ray irradiated water by photographing the ultra-violet absorption spectra of the irradiated water. His results showed that the initial excess of hydrogen could probably be accounted for by the production of hydrogen peroxide. Prompted by the work of Risse and Fricke on the stability of air-free water to X-rays, Nurnberger (24) re-investigated the alpha ray decomposition of air-free water. He took special precautions to remove dissolved air and eliminate traces of impurities from the water. These experiments proved that initially the gas evolved is 100% hydrogen, whereas later it is a mixture of hydrogen and oxygen. This was the first time that hydrogen gas had been reported as 100% in excess of an electrolytic mixture. In previous work, the observed excess was not more than 50%, which Nurnberger attributed to the presence of dissolved oxygen. He concluded that pure air-free water is decomposed by alpha rays and that dissolved oxygen is not necessary for the reaction.

Lanning and Lind (25) in 1938 studied the alpha ray decomposition of water with a view to using this reaction as a means of calibrating alpha ray bulbs containing radon. They studied this reaction by both the direct and indirect methods, previously described by Nurnberger. In the former, they applied corrections for (i) distribution of radon between liquid and gas phases, and (ii) recombination of hydrogen and oxygen in the gas phase by alpha particle bombardment, and calculated an ionic yield (M/N) of 0.716 for the decomposition of water. The alpha ray bulb used in the indirect experiments was calibrated using the ionic yield for the decomposition of ammonia by alpha particles established by Jungers (26). From these experiments Lanning and Lind calculated the ionic yield for the decomposition of water to be 0.868. They concluded that the true value of the ionic yield for the decomposition of water is very close to unity and that the net reaction is the decomposition of one molecule of water into hydrogen and nascent oxygen per ion pair.

In contrast with the earlier work of Risse and Fricke, Günther and Holzapfel (27) in 1939 reported that the X-ray irradiation of pure air-free liquid water, at room temperature, results in the formation of hydrogen. The number of hydrogen molecules formed was found to be of the same order as the number of ion pairs produced. However, it is well to note that Günther and Holzapfel used liquid hydrogen in their traps when purifying their water. At the temperature of liquid hydrogen, it is doubtful whether all the dissolved oxygen would be removed. Hence Günther and Holzapfel were probably studying the decomposition of water containing traces of oxygen. They also reported that ice at -180°C was not decomposed by X-irradiation.

Recently Allen (28), working on the United States Atomic Energy Project, has published a report on the effect of various types of radiation on pure water. In collaboration with J. A. Ghormley, he has shown that on irradiation with one m.e.v. electrons or X-rays from a Van de Graaff generator, a steady state of hydrogen and hydrogen peroxide is reached at levels of the order of a few micromoles per liter (hydrogen at a pressure of 1 to 2 cm. of mercury). They found that the steady state concentration increased with increasing intensity of radiation. Allen suggested that the difference between the effects of alpha rays and X-rays on pure water might be attributed to a difference in the steady state concentrations of the products characteristic of the two types of radiation.

With pile radiation, which consists of fast neutrons and gamma rays, steady states were obtained at hydrogen pressures of the order of 30 to 100 cm. These results were found to be extremely irreproducible because of the influence of dissolved or colloidal material coming from the walls of the fused silica vessels used.

They also studied water irradiated with deuteron beams from a cyclotron. The initial yield for the decomposition was found to be 0.54 molecules per 100 ev absorbed. With one atmosphere of electrolytic gas over the water, the yield was less than 0.1 molecules per 100 ev, suggesting that with this type of radiation the steady state concentration is just slightly greater than one atmosphere pressure.

In addition, Ghormley and Allen (29) have studied the decomposition of water in which part of the hydrogen had been replaced by its radioactive isotope, tritium. Tritium decays by beta ray emission, the average energy of the beta ray being about 5 k.e.v. In preliminary experiments they found that the steady state occurs around 10 to 20 cm. of hydrogen gas over the water.

On the basis of their experimental findings with 1 m.e.v. electrons, 5 k.e.v. electrons and cyclotron deuterons, Allen and coworkers concluded that the value of the steady state pressure appears to be correlated with the linear ion density of the charged particle which is responsible for the decomposition.

(B) AQUEOUS SOLUTIONS

Much experimental work is recorded in the literature on the chemical effects produced by ionizing radiations absorbed in aqueous solution. In the very early literature, the results are mostly of qualitative interest only. Where quantitative methods have been applied exact chemical analysis and radiation dosimetry were not always possible.

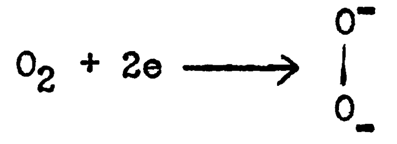
In general, it has been observed that aqueous solutions of inorganic solutes are oxidized or reduced, while organic solutes are oxidized or completely decomposed with the evolution of hydrogen and carbon dioxide.

(a) Aerated Water

Risse (19) in 1929 showed that pure air-free water is not decomposed by X-rays. He demonstrated that the formation of hydrogen peroxide in water irradiated with X-rays resulted from the combination of dissolved oxygen gas with 'activated water'. Subsequently, Fricke (20) confirmed the results of Risse and made an intensive study of the reduction of oxygen to hydrogen peroxide by irradiation of its aqueous solution with X-rays (30). With X-rays of 0.36 Å effective wavelength, he observed that the initial hydrogen peroxide yield was 2.2 micromole per liter per 1000 r, independent of the oxygen concentration from 9×10^{-6} to 16×10^{-4} M and independent of pH from 3 to 8. Above pH 8 the yield of hydrogen peroxide decreased and reached a limiting value approximately one-half the yield at low pH. In this connection, it is interesting to note that H_2SO_4 and H_3PO_4 gave similar results, whereas HCl and HNO_3 had a specific influence. In the pH range 7.5 to 9.0 a borate buffer was used and in a later study Fricke (21) reports that "the borate and phosphate ions were not always indifferent".

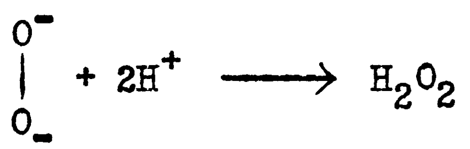
Previously, Fricke and Brownscombe (31) had found that X-ray irradiation of air-saturated 0.8 N H_2SO_4 formed hydrogen peroxide with a yield of 1.66 micromole per liter per 1000 r. However, this yield was obtained from the results for the reduction of dichromate solutions and cannot be favourably compared with the later work of Fricke.

In the early 1940's a number of papers on the radiation chemistry of water were published from the Institut du Radium in Paris. A paper by Loiseleur, Latarjet and Caillot (32) stressed the role of dissolved oxygen in the formation of hydrogen peroxide in water irradiated with X-rays. In their experiments, the water was heavily buffered (Clark and Lubs buffer) to maintain an accurately known pH. They used low energy, high intensity (17.5 kv. at 36 mA.) X-rays, expressing the radiation intensity in terms of the intensity at the surface of the water. Since it is necessary to know the amount of energy actually absorbed by the water to calculate yields, it is not possible to compare accurately their work with Fricke's. Nevertheless, they attributed the formation of hydrogen peroxide in aerated water to a direct primary activation of the oxygen molecule,



$$O_2 + 2e \longrightarrow \begin{matrix} O^- \\ | \\ O_- \end{matrix} ,$$

forming a doubly charged oxygen molecular ion, followed by a secondary reaction with H^+ ions



$$\begin{matrix} O^- \\ | \\ O_- \end{matrix} + 2H^+ \longrightarrow H_2O_2$$

The direct activation of an oxygen molecule seems highly improbable in view of the very small concentration of oxygen dissolved in aerated water, even at saturation ($\sim 3 \times 10^{-4}$ M).

Latarjet (33) in 1942 on the basis of an analogy between the effects of ionizing radiations and electrolysis proposed the following mechanism. The primary process was assumed to be a direct activation of an oxygen molecule by the radiation.

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2$$

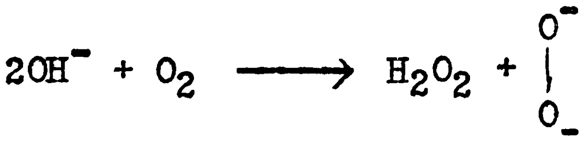
This results in an excess of hydroxyl ions which combine as

$$2OH^- - 2e \longrightarrow H_2O_2$$

Since the H^+ and OH^- ions result from the ionization of a water molecule, the overall reaction is written,

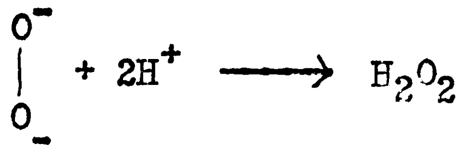
$$2H_2O + O_2 \longrightarrow 2H_2O_2$$

Loiseleur (34) observed a decrease in the pH of irradiated water containing dissolved oxygen, in the absence of any added buffer. Hence, he assumed that the primary effect of the radiation was to transfer an electron from each of two hydroxyl ions to an oxygen molecule,



$$2OH^- + O_2 \longrightarrow H_2O_2 + \begin{array}{c} O^- \\ | \\ O_- \end{array}$$

The oxygen molecular ion then reacted with H^+ ion to form hydrogen peroxide.



$$\begin{array}{c} O^- \\ | \\ O_- \end{array} + 2H^+ \longrightarrow H_2O_2$$

It is of interest to note that Latarjet and Loiseleur observed the formation of hydrogen peroxide in air-free water, i.e., water which had been boiled for 20 minutes.

Recently, Bonet-Maury and Lefort (35) re-investigated the formation of hydrogen peroxide in water irradiated with X-rays and alpha rays. They observed that for a given dose of X-rays the amount of hydrogen peroxide formed depends markedly on the dissolved oxygen concentration, whereas the yield of hydrogen peroxide in water irradiated with alpha rays was independent of the presence or absence of dissolved oxygen. In oxygen-saturated water, they found the formation of hydrogen peroxide by X-rays to decrease with temperature, a definite discontinuity marking the passage from liquid water to ice. Below -116°C peroxide could not be detected. With alpha particle irradiation (dissolved radon) they found no temperature coefficient for the formation of hydrogen peroxide in water. However, at the transition point from water to ice, a discontinuity was observed.

(b) Inorganic Solutes

In general, it has been found that aqueous solutions of inorganic solutes, irradiated with ionizing radiations, are oxidized or reduced. Those solutes which appear to be unaffected probably catalyze the decomposition of water.

In 1933, Fricke and Brownscombe (31) studied exhaustively the reduction of dichromate ion irradiated with X-rays, in aerated aqueous sulfuric acid solution. They observed that in 0.8 N H_2SO_4, the amount of reduction was proportional to the dose and independent of dichromate concentration between 2×10^{-3} N and 1.1×10^{-4} N. The initial yield for the reduction, 3.31 microequivalents per liter per 1000 r was the same as the initial yield for the formation of hydrogen peroxide. They observed a striking dependence of the reduction yield on pH. At low acidities the reduction yield was decreased; between 10^{-3} N and 10^{-4} N acid no reduction was observed. This was attributed to catalytic decomposition by the dichromate ion of the hydrogen peroxide formed during the irradiation. They found that the addition of traces of inorganic solutes, such as $(NH_4)_2SO_4$, $HgSO_4$ and $Fe_2(SO_4)_3$ had no effect on the yield, whereas the addition of trace amounts of organic acids, aldehydes or alcohols increased the reduction yield. This enhanced reduction was attributed by Fricke to the increased formation of hydrogen peroxide in the presence of the organic molecule.

In 1935, Fricke and Hart (36, 37) observed that irradiation with X-rays (0.36 Å) of gas-free dilute aqueous solution of ferrocyanide, arsenite, selenite and nitrite ion causes their oxidation and the evolution of an equivalent amount of hydrogen. In each case the oxidation yield was 0.55 micromole per liter per 1000 r, independent of the solute concentration from 10^{-4} M to 10^{-1} M and of pH from 2 to 11. On the basis of these data Fricke (38) concluded that the mechanism of these reactions are similar and due to the formation of activated water molecules, produced with a yield of 0.55 micromole per liter per 1000 r.

Clark and Coe (39) in 1937 studied the reduction of aerated aqueous ceric sulfate solutions irradiated with X-rays (0.60 Å). Their experiments showed that the initial reduction yield was independent of the ceric sulfate concentration between 2×10^{-4} M and 4×10^{-4} M.

There was no marked effect of pH; however, increasing the acid concentration from 0.05 N to 1.2 N decreased the reduction yield by approximately 10%. They found that the addition of organic materials increased the reduction yield.

Clark and Coe also studied the reduction of aqueous solutions of potassium permanganate. The reaction products observed were found to be strongly dependent on acid concentration. In solutions less than 0.1 N H_2SO_4, MnO_2 is formed, whereas at higher acidities (1.0 N) Mn^{++} ion is formed.

In 1935 Fricke and Hart (40) studied the effect of iodide and bromide ion on the decomposition of air-free water. For halide concentrations from 10^{-5} M to 10^{-3}M, free halogen was not found. However, they observed the formation of hydrogen peroxide with the simultaneous evolution of hydrogen. The yield of hydrogen peroxide, 0.55 micromoles per liter per 1000 r, was found to be independent of the halide concentration between 10^{-5} M and 10^{-3} M in the presence of H_2SO_4 at pH 3. For lower concentrations of halide ion (less than 10^{-5} M) the yield of hydrogen peroxide decreased, while at high concentrations of halide (greater than 10^{-3} M) the formation of free halogen was observed. A similar catalytic phenomenon with chloride ion was not observed.

Recently, Allen (28) has reported that using fast electron beams, the bromide ion increases the steady state concentration of hydrogen peroxide and hydrogen gas. He gives a value of 40 cm. (of mercury pressure) of electrolytic gas over a solution 4 x 10^{-5} M in KBr. He reports similar effects with HCl and HNO_3 at concentrations of 0.01 N. However, H_2SO_4 and H_3PO_4 at the same concentration did not increase the steady state very much beyond the value for pure water.

(c) Ferrous Sulfate

The first quantitative study of the oxidation of ferrous ions by high energy radiations was reported by Fricke and Morse (41) in 1927, who investigated the effect of X-ray wave-length on the oxidation yield. Their irradiation vessels were made from a piece of solid glass in which a hole was drilled, each side being sealed air-tight with cover glasses 0.1 mm. thick. Cells of different diameters and thicknesses were used. However the one most employed had a diameter of 3 cm. and a thickness of 2.5 mm. The solutions were analyzed electrometrically by adding an excess of sodium bichromate and back-titrating with ferrous sulfate. The dose was determined with a thimble type graphite ionization chamber (volume 0.1 cc.). The effect of wave-length was investigated with an aerated solution 10^{-3} M in ferrous sulfate and 0.8 N in sulfuric acid. They found the amount of oxidation to be directly proportional to the dose, and that for a given dose the amount of chemical change was independent of the wave-length from 0.204 Å to 0.765 Å, when the dose is measured in roentgens with the cell filled with air.

Fricke and Morse (42) continued their study of this reaction with a view to developing it as a radiation chemical dosimeter. They were particularly interested in examining the behaviour of a 4×10^{-5} M solution of ferrous sulfate which would, on the basis of their earlier results, be 50% oxidized by a dose of 1000 roentgens and would consequently be of value in radiotherapeutic dosimetry. The solutions were aerated and made 0.8 N in sulfuric acid. They found the amount of oxidation to be a linear function of the dose and that when all the ferrous ions are oxidized an equivalent amount of hydrogen peroxide or of a similar substance accumulates which can be titrated with sodium bichromate. They state that the temperature coefficient of this reaction must be quite low, since fairly large fluctuations in the temperature of the irradiation room did not produce any detectable change in the yield.

At a meeting of the American Physical Society in 1928, Fricke (43) reported that the amount of ferrous sulfate oxidized for a given dose of X-rays was independent of the ferrous sulfate concentration from 10^{-2} M to 4 x 10^{-5} M in 0.8 N sulfuric acid solution. Thus he concluded that the oxidation is due to a primary production of activated water molecules. For solutions containing dissolved oxygen he found that 8.2 (± 2%) ferrous ions were oxidized per activated water molecule formed, and that 2.05 oxygen molecules were simultaneously reduced. In gas-free solutions 4.1 ferrous ions were oxidized. However these calculations were based on Duane and Scheuer's determination of the number of water molecules transformed to hydrogen and oxygen by alpha rays which is not applicable to this problem.

In their classical paper of 1929 Fricke and Morse (44) gave a detailed account of their work on the oxidation of ferrous ions by X-rays. The experimental techniques were similar to those described above. All irradiations were made with 100 kv (40 mA) X-rays, and the solutions were saturated with atmospheric air and contained 0.8 N sulfuric acid. At all concentrations studied they observed a linear oxidation of ferrous ion with dose, as long as a certain dose was not exceeded, and within this range the absolute amount of oxidation for a given dose was independent of the ferrous ion concentration. At a certain critical dose the yield was suddenly decreased by a factor of two, but the percent oxidation was still a linear function of the dose. This sudden break in the curve they attributed to complete removal of dissolved oxygen, since at the break the number of ferrous ions oxidized was equal to the number of equivalents of dissolved oxygen.

To obtain information about hydrogen peroxide as a possible intermediate in the reaction, they irradiated 0.8 N sulfuric acid and added it to the ferrous sulfate solution. Even though their results were very irregular, they found effects comparable with those obtained by direct irradiation of a ferrous sulfate solution which does not contain dissolved oxygen. They also observed an apparent radiation equilibrium at about 94% oxidation, which indicated that ferric ions were reduced by X-rays.

In 1932 a paper by Shishacow (45) from the Roentgen Institute, Moscow, criticized the electrometric titration method used by Fricke and Morse for the analysis of their ferrous solutions. Shishacow objected to their standard electrode (a Pt wire in a half-oxidized 10^{-1} M solution of ferrous sulfate) because this led to increased spontaneous oxidation of the ferrous ion. He also objected to their use of +150 millivolts as the potential for the end-point at all concentrations because his own experiments had shown the end-point potential to depend on the concentration. Shishacow elected to use the normal calomel electrode as his standard. He found that the oxidation of a 2×10^{-3} M solution (surface of the liquid in contact with air), 0.8 N in sulfuric acid, was quantitative, and that the yield was the same as that found by Fricke and Morse. In confirmation of the fact that the ferrous ion was quantitatively oxidized, he found that ferric ion solutions, 10^{-3} M to 5×10^{-2} M, were not reduced by X-rays. He also found a very long induction period with a boiled solution which had been saturated with hydrogen.

A more detailed study of the oxidation of ferrous sulfate in aqueous solution by X-rays was reported by Fricke and Hart (46) in 1935. They confirmed the earlier result that the amount of ferrous ion oxidized in 0.8 N sulfuric acid was directly proportional to the dose, and also that the oxidation yield was independent of the initial ferrous concentration from 10^{-2} M to 4×10^{-5} M. By Van Slyke analysis of the gas produced from air-free solutions, they found that hydrogen gas was formed in amount approximately equal to one-half the number of ferrous ions oxidized. With aerated solutions, hydrogen was not found, but they were able to show that four ferrous ions were oxidized for every oxygen molecule consumed. They found the reaction in both aerated and air-free solution to be dependent on pH (from pH 1 to pH 3) and independent of sulfate concentration when the solution was made 0.4 M in sodium sulfate. The yield was also found to be independent of the partial pressure of oxygen from 70 cm. to 4 cm. of mercury, Nurnberger (22) in 1934, in a study of the effect of alpha particles on water and aqueous solution, investigated the oxidation of ferrous sulfate. This is the only reported study of this reaction with heavy particle radiation. Nurnberger was particularly interested in determining the behaviour of the excess hydrogen during the course of the reaction. He used the previously described direct and indirect methods of irradiation. The solutions were stirred continuously at constant temperature. The amount of ferrous sulfate oxidized was followed by electrometric titration. He observed, in marked contrast to the results with pure water, that the gas evolved during the reaction was almost 100% hydrogen. He found the amount of ferrous sulfate oxidized to be directly proportional to the dose when radon was dissolved in the solution (direct method), but observed slight deviations from a straight line using the alpha ray bulb (indirect method). His curves showed the reaction to be quantitative. The yield for the oxidation of ferrous ion was found to decrease with decrease in the initial ferrous sulfate concentration and appeared to approach a constant value for dilute solutions (4.5×10^{-3} M). The yields obtained by the indirect method were in nearly every case 50% greater than by the direct method.

Liechti, Minder and Wegmuller (47) in 1945 studied the oxidation of ferrous ions in aqueous solution by X- and γ-rays. Their irradiation cell was simply a glass tube in which a radium source, contained in a cylindrical coaxial vessel, was placed. They assumed that the dose distribution on the inside of the cylinder was largely homogeneous and gave an equation which enabled them to calculate the dose. The disappearance of ferrous ion was determined by titration with dilute potassium permanganate with an estimated average error of ± 3%. In agreement with earlier work they found that the number of ferrous ions decreased linearly with dose, to complete oxidation. They give the following reaction to account for the oxidation,

$$Fe^{+2} + H_2O \longrightarrow Fe(OH)^{+2} + H^+$$

from which they concluded that the reaction should be dependent on pH; however, this equation is not electrically balanced. They did, in fact, find that the reaction was strongly dependent on pH. Unfortunately in their paper they do not specify the concentrations of sulfuric acid used. The yield was reported to be 2.4 times greater in the presence of free sulfuric acid than in the absence of acid. In neutral solution they observed that all the oxidized iron was precipitated in the form of basic sulfate, which led them to suggest the following reaction,

$$4Fe^{+2} + 4SO_4^{=} + 2H_2O + O_2 \longrightarrow 4FeSO_4(OH)$$

They indicate that this is evidence for the formation of OH in irradiated water. In marked contrast to the results of Fricke and coworkers, they did not observe any oxidation in the absence of dissolved oxygen (a solution boiled out under vacuum).

In the following year Minder and Liechti (48) published a paper on the influence of temperature on the γ-ray induced oxidation of ferrous sulfate, The experimental technique was the same as that used by Liechti, Minder and Wegmuller. Between 4° and 54°C they found the oxidation yield to be independent of temperature at a ferrous ion concentration of 2 x 10^{-3} M acidified with sulfuric acid (concentration not specified). No measurable oxidation was observed with a solution frozen in solid carbon dioxide.

Miller (49) in 1948 published a note on the oxidation of ferrous ion in aqueous solution by X- and γ-radiation with a view to establishing the absolute yield for the reaction. The solutions were prepared from carefully purified water and were made 0.8 N in sulfuric acid. Ferrous ion was analyzed by potentiometric titration with dilute ceric sulfate solution. He found that the oxidation yield was independent of the concentration of ferrous ions between 10^{-3} M and 10^{-4} M and also that the yield was independent of the wave-length of the radiation, using 200 kv. X-rays and the γ-rays of radium. In addition, he found that very little oxygen was necessary to saturate the solution effectively with oxygen, from a radiation chemical point of view, provided high doses of radiation were not used. In his work, Miller never used doses greater than 13,000 roentgen. He also found that preliminary evacuation of the solution for twenty or thirty minutes decreased the yield by a factor of 2.5. Expressed as the number of ferrous ions oxidized per 32.5 ev expended in the solution, the average oxidation yield for solutions containing dissolved oxygen was 6.0.

A very recent unclassified report from the University of California by Todd and Whitcher (50) presents the results of a study of the action of X-rays on solutions containing iron. The reaction was followed by analyzing for ferric ion by the thiocyanate method. The solutions were made with carefully purified water and contained 0.8 N sulfuric acid. Samples were irradiated in a 40 cc. spherical pyrex cell placed in the center of the unfiltered radiation field of a 250 kv Picker X-ray tube at a distance of 25 cm. from the focal spot. The cell was rotated slowly to give the sample a uniform dose. In agreement with previous workers, they found the amount of chemical change proportional to the energy absorbed by the solution. The yield was observed to be independent of X-ray intensity from 10 r/min. to 500 r/min. They found that the ferrous ion is completely oxidized, which indicated no reduction of the ferric ion. This was confirmed by irradiation of ferric solutions. A plot of the oxidation yield vs. ferrous ion concentration indicated that the yield decreased below a ferrous ion concentration of 10^{-3} M.

Miller (51) has recently published a comprehensive report of his studies on the ferrous sulfate system. He was particularly interested in the applicability of this system as a chemical dosimeter in radiation chemical studies. Following the cavity principle developed by Bragg and Gray, Miller has shown that this system meets all the requirements of a chemical dosimeter. Accordingly he has made precise measurements of the yield under different experimental conditions, and concluded that the oxidation yield was 6.7 Fe^{+2} ions oxidized per 32.5 ev expended in the solution.

Miller also observed that the oxidation yield was the same for air-saturated and oxygen-saturated solutions. With air-saturated and oxygen-saturated solutions, in the absence of a gas phase, he observed that a sharp break in the oxidation occurred at 45,000 r and 218,000 r respectively. By assuming that the break occurred when all the oxygen had been removed, it was found that one equivalent of oxygen was removed for each equivalent of Fe^{+2} ion oxidized. In addition, it was found that lower oxidation yields were obtained with solutions saturated with (i) nitrogen, containing less than one-half percent of oxygen and (ii) hydrogen. He has further shown that evacuating the solutions reduced the oxidation yield by a factor of approximately 2.5. However, the results obtained were not reproducible, which Miller attributed to incomplete deaeration.

(C) THEORETICAL

The mechanism of the chemical action of high energy radiations absorbed in water and dilute aqueous solutions has been the subject of considerable speculation.

In the preceeding discussion of the chemical effects produced by high energy radiations absorbed in aqueous solution of inorganic ions, it was, in general, observed that (i) at low solute concentrations the initial yield was independent of the solute concentration over a wide range, and (ii) the amount of solute changed was directly proportional to the energy absorbed in the solution.

Risse (19) in 1929 observed these effects in a study of the X-ray induced decomposition of hydrogen peroxide in dilute aqueous solution. On the basis of these results he was led to the conclusion that the primary action of the radiation on aqueous solution is the formation of 'activated water' molecules, followed by transfer of energy to the solute by inelastic collision. This hypothesis was later accepted and extended by Fricke and co-workers (38) in their numerous researches on the action of X-rays on water and aqueous solutions. This work added considerably to the plausibility of the 'activated water' hypothesis. From his results, Fricke was of the opinion that there were two species of activated water. One species was always produced in water, whereas the second species had the specific ability of bringing oxygen, dissolved in the water, into a highly reactive state. This conclusion was based on an experimental study of the oxidation of Fe^{+2} ions both in the presence and absence of dissolved oxygen, for it was found that in the presence of dissolved oxygen the oxidation yield was greatly enhanced. Fricke was greatly concerned with the mean lifetime of this 'activated water' molecule. He was able to obtain a value for the mean lifetime from the study of a suitable reaction, at concentrations low enough that the yield had decreased, i.e., at solute concentrations such that the activated water molecule does not encounter a solute molecule before it is eliminated. The system he chose to study was the decomposition of pure water in the presence of iodide ion. In this system, the initial yield was found to decrease at concentrations below 0.01 milliequivalents per liter and Fricke concluded that 'activated water' has a lifetime of approximately 10^{-5} sec. Such a long lifetime led Fricke to speculate as to the probable nature of these 'activated water' molecules. In fact, he had originally believed (52) that the absorption of X-rays would simply result in dissociation of the water molecule. This however, he concluded to be an improbable assumption, since X-rays did not decompose water.

It is interesting to note that at the Cold Spring Harbour Symposium in 1935, Kassel (38) suggested that if water were dissociated into H and OH by X-rays, it would be reasonable to suppose that, if H atoms did not recombine in aqueous solution, then the OH would combine in pairs to give hydrogen peroxide. However, the excess H atoms would immediately react with the hydrogen peroxide regenerating water, hence there would be no net decomposition. In connection with the probable nature of 'activated water' it is also noteworthy that at the Cold Spring Harbour Symposium in 1938, Fricke (53) stated, "the nature of the chemically active particles produced by the action of X-rays on water is not completely certain. Probably we are dealing with dissociation products (particularly H and OH) of the water molecule, but there is still some difficulty in accounting for all the observations on this basis".

Early in 1940, the 'activated water' hypothesis received further confirmation from the delicate experiments of Dale (54) on the inactivation of enzymes by X-rays in dilute aqueous solution. Prior to his experiments, it was generally believed that enzymes were inactivated only by extremely large doses of radiation. However, working with a highly purified enzyme (carboxypeptidase in the absence of its substrate) in pure aqueous solution, Dale was able to show that inactivation occurred with very small doses of radiation, of the order of 100 roentgens or less. His results clearly showed that for a given amount of energy absorbed in the solution, a constant amount of enzyme was inactivated irrespective of the enzyme concentration. In confirmatio of earlier work, he found that no inactivation occurred if the enzyme was irradiated in the presence of its substrate. Subsequently, he found this inhibitory effect to be a general feature of enzyme inactivation by X-rays. From this, he concluded that if more than one solute were present each would compete for the activated intermediate according to its amount and its affinity for 'activated water'. A similar explanation was advanced to account for the exponential inactivation of enzymes, for he assumed that the inactivated solute could act as a protective agent (55, 56).

To account for the various chemical effects produced by X-rays absorbed in dilute aqueous solution, Weiss (57) in 1944 proposed that the overall primary radiochemical process in water was the formation of H atoms and OH radicals. This suggestion was based on knowledge obtained from the electron transfer spectrum of ions in aqueous solution. These spectra were attributed to the transfer of an electron to (or from) an ion to a neighbouring water molecule. The spectra of many simple and complex ions investigated in the far ultra violet give bands which, from their intensity and position, can be interpreted as electron transfer bands. By an extension of this view, Weiss reasoned that since water is composed of H^+ ions and OH^- ions, the absorption of radiation by the OH^- ion would result in the transfer of an electron to a neighbouring H^+ ion, and wrote the radiochemical primary process as

$$(HO)^- H^+ \xrightarrow{X,\gamma,\alpha\ldots} OH + H$$

or

$$(HO)^- H_2O \xrightarrow{X,\gamma,\alpha\ldots} OH + H + OH^-$$

To account for the radiation stability of water, he pointed out that the recombination reaction

$$H + OH \longrightarrow H_2O$$

would be especially favoured in solution because the primary dissociation products are held together by the surrounding water molecules (Franck-Rabinowitch cage effect). The ability of the H atom to donate an electron to, and of the OH radical to accept an electron from, a solute dissolved in the water accounted for the well known oxidizing and reducing properties of irradiated water. For example, he explained the oxidation of Fe^{+2} ions by the reaction,

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^-$$

resulting in an excess of H atoms which, in the absence of dissolved oxygen, would combine to form molecular hydrogen.

A more comprehensive discussion of the primary and secondary processes in irradiated water will be given in the following sections.

PRIMARY PROCESS

It is now generally accepted that the free radical hypothesis accounts for the properties of 'activated water', but this has undergone considerable extension, notably in the hands of Lea (58), Allen (59), Dainton (60) and others.

The simple electron transfer process suggested by Weiss to explain free radical production in irradiated water is generally believed to be incomplete and a more rigorous picture of the mechanism has been given by Lea (58).

From a consideration of the physics of the interaction of high energy radiations with matter, Lea believed that the truly primary process would be ionization of the water molecule with the ejection of a fast secondary electron. Thus he wrote the primary process in water as,

$$H_2O \xrightarrow{X,\gamma,\alpha\ldots} H_2O^+ + e$$

The H_2O^+ ion is well known from mass spectrographic studies on irradiated water vapour (61). In water, the H_2O^+ ion will rapidly react with a water molecule to give an OH radical.

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

This reaction is several electron volts exothermic due to the high hydration energy of the proton. Consequently, the H_2O^+ ion will have an extremely short lifetime in liquid water, and an OH radical will remain at the site of the ionization.

The electron ejected in the primary process may have considerable energy which will probably be lost in further ionization. Hence, on the average, such electrons will travel some distance before their energy is reduced to the order of thermal energies, when they will be captured. Capture by a water molecule results in the reaction,

$$H_2O + e \longrightarrow H_2O^-$$

If the H_2O^- ion decomposes immediately, the reaction

$$H_2O^-_{aq} \longrightarrow H + OH^-_{aq}$$

will produce an H atom at the site of electron capture. This reaction is very exothermic due to the high hydration energy of the hydroxyl ion. In addition, this reaction will be aided by the much higher electron affinity of the hydroxyl group compared with that of the water molecule.

Thus the overall picture will be the production of H atoms and OH radicals with, in general, a distribution which will be determined by the linear ion density of the ionizing particle.

In addition to ionization it is well known that high energy radiations absorbed in matter can also produce excitation. The evidence for this comes from the experimental observation that the energy required to form an ion pair in gases is approximately twice the ionization energy of the gas (62). It is concluded that a comparable amount of energy is spent in excitation processes. With water, excitation may lead directly to dissociation of the water molecule into H atoms and OH radicals. Lea believes that H and OH formed in this process will immediately recombine, since they will be formed in a cage of water molecules and sufficient energy will be removed by the surrounding water molecules before the H and OH can diffuse an appreciable distance. On the other hand, Dainton (60) states that the exchange reaction,

$$OH + H_2O \longrightarrow H_2O + OH$$

will enable an OH radical to escape from its cage of water molecules before recombination. Recent experiments by Dainton (63) have, in fact, shown that this reaction does occur, but not with an exceptional velocity.

Direct physical evidence in support of this free radical theory has not as yet been obtained. However, indirect experimental evidence has recently been reported in the literature. For example, Dainton (64) has found that irradiation with X- and γ-rays of dilute aqueous solutions of acrylonitrile and methacrylonitrile causes polymerization of the solute. These solutions are known to be stable to high concentrations of H_3O^+ and OH^- ions and it is also known that OH radicals produced by the Fenton reaction,

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+2} + OH^- + OH$$

can initiate polymerization of these materials in aqueous solution (65). In addition, Dainton has found the OH group vibration frequency in the infra red absorption spectra of the dry polymers. Somewhat similar evidence has been reported by Weiss and Stein (66). They observed that irradiation with X-rays of a dilute aqueous solution of benzene resulted in the production of phenol. They concluded that hydroxylation results from the formation of OH radicals by irradiation of water with X-rays.

SECONDARY PROCESSES

In pure air-free water the production of H and OH will result in three possible reactions, namely,

$$H + OH \longrightarrow H_2O \qquad (1)$$

$$H + H \longrightarrow H_2 \qquad (2)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (3)$$

All these reactions are appreciably exothermic and the excess of energy will be rapidly removed by the proximity of the surrounding water molecules. Reactions (1) and (2) are thought to have negligible activation energies. Weiss (67), however, suggested that reaction (3) may require an appreciable activation energy because of the large dipole repulsion forces between the hydroxyl radicals. Nevertheless, it is probable that this activation energy will be much reduced by hydration of the hydroxyl radical which will permit close approach of two hydroxyl radicals. It is highly probable that there is hydration of the hydroxyl radical simply because it possesses a strong dipole.

Decomposition of the water will only be observed under conditions such that the combination of like radicals is considerably more probable than recombination of unlike radicals. In pure water this will be largely determined by the spatial distribution of the radicals. Thus with light particle irradiation (X- and γ-rays) the uniform distribution of radicals will favour recombination of H and OH. The dense columnar ionization of heavy particle irradiation (protons and α-particles) will favour combination of like radicals in the track of the ionizing particle. These conclusions readily account for the experimental observations that X-rays give little or no decomposition of pure water, while α-particles give appreciable amounts of decomposition products (28).

The presence of dissolved oxygen greatly enhances the yield of hydrogen peroxide in the X-ray irradiation of water. This has been attributed to the formation of the perhydroxyl radical in the reaction

$$H + O_2 \longrightarrow HO_2$$

In the gas phase this reaction is exothermic to the extent of about 60 kcal. and hence will require the presence of a third body (68). In liquid water this requirement is already met, consequently the perhydroxyl radical may have an appreciable lifetime. Hydrogen peroxide may form in the following reaction,

$$H + HO_2 \longrightarrow H_2O_2$$

or in the presence of a large excess of dissolved oxygen by the dismutation

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

The decomposition products H_2 and H_2O_2 are readily attacked by the H and OH and after a sufficient concentration of products has formed the following back reactions may occur,

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$

$$OH + H_2 \longrightarrow H_2O + H$$

$$H + H_2O_2 \longrightarrow H_2O + OH$$

$$HO_2 + H_2O_2 \longrightarrow H_2O + OH + O_2$$

Consequently, a steady state concentration of products results which is characteristic of the radiation intensity and type of radiation used. The system H_2O-OH-H-HO_2-H_2O_2-O_2 is extremely complicated and a completely satisfactory system of kinetics has not as yet been worked out.

KINETICS OF INDIRECT ACTION

The most outstanding feature of radiation induced reactions in dilute aqueous solution is the linear relation generally observed between the number of molecules reacted and the energy absorbed by the solution. This relation immediately suggests that the yield, which is the slope at any point on the curve, is independent of the solute concentration. The direct consequence of such an observation is that the agent responsible for the observed chemical effects must be formed in the water medium, i.e., indirect action. That is, the solute molecules have not been ionized or excited directly, but their reaction is a consequence of the formation of H and OH in the water.

Several attempts have been made to explain certain aspects of the kinetics of indirect action, such as the dependence of the yield on solute concentration, dose rate, linear ion density and other variables.

Weiss (57) using the steady state concept, worked out a simple system of kinetics to account for indirect action. He considered the following scheme,

$$H_2O \xrightarrow{X..} H + OH$$
$$S + OH \xrightarrow{k_1} H_2O$$
$$H + OH \xrightarrow{k_2} \text{Product}$$

where S is the solute molecule. Let I be the dose rate in ev sec^{-1} per unit volume, k be the number of free radical pairs formed per ev, k_1 be the velocity constant for the removal of radicals on collision with the solute and k_2 be the velocity constant for recombination of unlike radicals. At the stationary state, the rate of production of radical OH will be

$$\frac{d(OH)}{dt} = kI - k_1(S)(OH) - k_2(H)(OH) = 0$$

from which

$$(OH) = \frac{kI}{k_1(S) + k_2(H)}$$

The rate of disappearance of solute will be

$$-\frac{d(S)}{dt} = k_1(S)(OH)$$

and substituting the value of (OH)

$$-\frac{d(S)}{dt} = \frac{k_1(S)\,kI}{k_1(S) + k_2(H)}$$

If it is assumed that recombination of unlike radicals does not occur, then $k_2(H)$ can be neglected and we have,

$$-\frac{d(S)}{dt} = kI \qquad \text{or} \qquad -\frac{d(S)}{Idt} = k$$

It is evident from this equation that a plot of solute reacted against energy absorbed will be a straight line of slope k. Consequently, this simple derivation is capable of accounting for the experimental observation that the amount of solute reacted is directly proportional to the energy absorbed.

A more rigorous approach has been given by Lea (58) who has been particularly concerned with evaluating the proportion of radicals uncombined after a given time as a result of diffusion from the original track. His approach to this problem is based on Jaffé's (69) study of the recombination of ions in particle columns. Lea assumes that the initial distribution of the radicals is the same as the initial distribution of the positive and negative ions, hence Jaffé's equation,

$$n = \frac{N_o}{\pi b^2} \cdot e^{-\frac{r^2}{b^2}} \qquad (1)$$

also gives the initial distribution of the radicals. In this equation, n is the number of radicals (H or OH) per unit volume, r is the distance from the track, N_o is the number of radicals (H or OH) per cm. path produced by the ionizing particle and b is a measure of the radius of the column of radicals. The validity of the application of this equation to represent the initial distribution of the radicals is based on the following assumptions, (i) that H_2O^+ is the only positive ion formed, (ii) radicals produced by excitation are not considered, (iii) radicals have only thermal energies and are in their ground states (60).

Shortly after the passage of the ionizing particle the radicals will have diffused out of their original track, and after a time t their distribution will be given by,

$$n = \frac{N}{\pi(4Dt + b^2)} \cdot e^{-r^2/(4Dt + b^2)} \qquad (2)$$

where D is the diffusion coefficient of the particular radical, and the radius of the column has increased from b to $(4Dt + b^2)^{1/2}$, N is the total number of radicals per cm. path at time t, its value being less than N_0 due to recombination of radicals and also their reaction with any solute present.

To test the applicability of these equations for the calculation of reaction rates, it was necessary to determine whether reaction occurred in general before or after the columns overlap. If most of the radicals in a column have disappeared by the time adjacent columns overlap, then each column may be considered an isolated entity and the concentration of radicals to be used in calculating reaction rates will be given by equations (1) or (2). However, if only a small proportion of the radicals have disappeared by the time adjacent columns overlap then the concentration of radicals will be obtained by dividing the total number of radicals by the total volume of the solution.

If I is the dose-rate in roentgens per second, then approximately $2 \times 10^{12}It$ ion pairs (hence also radical pairs) will be produced per cc. in t seconds. The factor 2×10^{12} expresses the number of ion pairs produced per roentgen per cc. in a medium of density unity. Since there are N_o radical pairs per cm. path, then the number of radicals which cross each square cm. in t seconds will be given by,

$$\frac{2 \times 10^{12} It}{N_o}$$

After a time t seconds, the radius of the column has increased to $(4Dt + b^2)^{1/2}$, and its area will be,

$$\pi(4Dt + b^2)$$

Therefore, for the columns to overlap in t seconds the relation,

$$\pi(4Dt + b^2) \times \frac{2 \times 10^{12} \times It}{N_o} = 1$$

must be satisfied. Since $4Dt \gg b^2$, the following expressions may be deduced,

$$t = 10^{-6} \times \left(\frac{N_o}{8\pi DI}\right)^{1/2} \qquad (3)$$

and

$$(4Dt + b^2)^{1/2} = 10^{-3} \times \left(\frac{2N_oD}{\pi I}\right)^{1/4} \qquad (4)$$

where equation (3) gives the time required for the columns to overlap, and equation (4) gives the radius of a column when adjacent columns overlap.

Lea has worked out typical numerical values, using the following values,

$I = 10$ r per second

$D = 2 \times 10^{-5}$ cm^2 sec^{-1}

$N_o = 3 \times 10^7$ ionizations per cm. for α-rays

$N_o = 6 \times 10^5$ ionizations per cm. for X-rays.

Substitution of these values in equation (3) and (4) show that for X-rays adjacent columns overlap after 0.01 seconds when the column radius is 0.001 cm. For α-rays, he finds that adjacent columns overlap after 0.08 second when the column radius is 0.0025 cm.

Consider the following recombination reaction as the only reaction responsible for elimination of the radicals,

$$H + OH \longrightarrow H_2O$$

The number of radical pairs disappearing per unit volume per second will be given by,

$$\alpha n^2$$

where n is the number of radicals per unit volume and α is a constant. The value of α, calculated on kinetic theory considerations assuming a probability of unity for the collision efficiency between H and OH, is taken to be 4×10^{-10}. The number of pairs of radicals N which remain uncombined after a time t is related to the original number N_o by the equation of Jaffé,

$$\frac{N_o}{N} = 1 + \frac{\alpha N_o}{8\pi D} \ln \frac{4Dt + b^2}{b^2} \qquad (5)$$

This equation has been evaluated by Lea using the values of α, N_o and D given above and the value for $b = 1.5 \times 10^{-6}$ cm. He finds that by the time the columns overlap the proportion of radicals remaining uncombined is 0.3% in an α-ray column and 13% in an X-ray column. It appears reasonable to suppose that in the presence of a solute that is reactive towards H and/or OH the radicals will disappear still more quickly. Thus Lea concluded that reaction takes place independently in the paths of each individual ionizing particle and that the radicals produced by the ionizing particles do not appreciably mix.

The numerical values used in the evaluation of these equations are subject to considerable uncertainty. In particular, the value taken for b in water (density 1.0) is an extrapolated value based on the value for $b = 1.79 \times 10^{-3}$ cm. in air (density 0.0012) and $b = 2.34 \times 10^{-6}$ cm. in hexane (density 0.677). In addition, the value for D is that for D_2O in water. However, it is very likely that the effective diffusion coefficient for H atoms, for example, in water is quite different from that measured for D_2O in water.

Although there is a paucity of direct physical evidence for the production of H and OH in water, their formation appears to be a logical consequence of the primary ionization act. A knowledge of the lifetimes of these entities in liquid water would be invaluable. It is evident from a consideration of the mechanism by which ionizing radiations interact with matter, that the lifetimes of these free radicals will be a function of the spatial distribution of the particular ionizing radiation. Lea has made provisional calculations of the lifetimes of these radicals on the basis of Jaffé's columnar recombination theory. However, his calculations are limited by uncertainties in the values for the diffusion coefficients of the radicals and the parameter b which is a measure of the radius of the column of radicals. He does calculate, however, that with α-particle radiation, one-half of the radicals have recombined in 1.2×10^{-9} sec. and 2×10^{-7} sec. with X-radiation. Further calculation by Lea (70) indicates that in an α-particle track the recombination of H and OH will be nearly complete by the time the column has diffused to a few times its initial radius. This implies, therefore, that the chemical effects produced by α-particles will occur mainly in or very near the α-particle track, and that there will be little interaction between radicals from different tracks.

A similar calculation for X-rays (70) indicates that in the track of a secondary electron of 10 - 20 kev energy, i.e., X-rays generated at 50 - 200 kv, the column of H atoms will have diffused to more than 100 times its initial radius before half of the radicals have recombined. Hence, the chemical effects produced in this case will not necessarily be confined to the individual electron tracks. It is necessary, however, to point out that the long wave-length X-rays (50 kev or less) give rise to considerable cluster formation. For example, with X-rays of wave-length 1.5 Å, the mechanism of energy absorption is primarily photoelectric. The energy of the photoelectron will be about 8 kev which has a range in water of 1.6 microns. Hence the ionization produced by these X-rays is not uniform but is localized along tracks. On the other hand, for 1.0 Mev γ-rays, the mechanism of energy absorption is almost entirely by the projection of Compton recoil electrons. In this case, the mean recoil electron energy will be about 450 kev which has a range of about 1500 microns in water. It would then be expected that the chemical effects produced by γ-radiation absorbed in water will occur uniformly throughout the irradiated zone. This treatment, however, does not take into account the change in ion density along the electron track as it dissipates its energy. Furthermore, it is questionable how rigorously a columnar theory can be applied to γ-radiation.

The treatment given by Lea is highly instructive in that it attempts to define the zone of chemical reaction and lifetimes of the H and OH. Furthermore, it stresses the importance of the spatial distribution of the radicals in relation to the efficiency of the chemical reaction induced by the ionizing radiation.

Recently, Dainton (63) has developed a kinetic scheme for indirect action in aqueous solution which predicts the dependence of the yield on solute concentration and dose rate. Let I be the dose rate (ev/W absorbed per unit volume per unit time) where W is the mean energy to create an ion pair, and k/2 be the net number of water molecules dissociated per W ev absorbed after allowance has been made for the almost instantaneous recombination of radicals by the Franck-Rabinowitch mechanism. Let the concentration of the solute be given by S, and k_1 be the rate constant for removal of the radicals by the solute. Thus, the rate of radical formation is given by,

$$\frac{dn}{dt} = 0.5kI - k_1nS - (k_3 + k_4)n^2$$

where n, the concentration of radicals, is initially non-uniform throughout the system, k_3 is the rate constant for recombination of unlike radicals, and k_4 is the rate constant for combination of like radicals in pairs to form H_2 or H_2O_2. The last term in this equation will be a function of the linear density of the ionizing particle, the distribution of H atoms and OH radicals in the track of the particle and the diffusion coefficients of the H and OH.

If p is the probability that in the radical-solute interaction the solute is destroyed, then the rate of reaction will be,

$$-\frac{dS}{dt} = pk_1Sn$$

and the ionic yield (M/N) will be,

$$\frac{M}{N} = \frac{pk_1nS}{I}$$

Two extreme cases are possible:

(a) $$k_1S \gg (k_3 + k_4)n$$

then the rate of reaction will be,

$$-\frac{dS}{dt} = 0.5pkI$$

and the rate is zero order with respect to the solute concentration, i.e., the amount of solute changed will be a linear function of the energy absorbed in the solution. In this case the yield will be,

$$\frac{M}{N} = 0.5pk$$

Hence under conditions such that $k_1S \gg (k_3 + k_4)n$, that is, at high concentrations of the solute, the yield will be independent of the solute concentration and also of the dose rate.

(b) $$k_1S \ll (k_3 + k_4)n$$

then the rate of reaction will be,

$$-\frac{dS}{dt} = pk_1S\left\{\frac{0.5kI}{(k_3 + k_4)}\right\}^{1/2}$$

and the rate is first order with respect to the solute concentration and proportional to the square root of the dose rate. In this case, then, the yield will be,

$$\frac{M}{N} = pk_1S\left\{\frac{0.5k}{I(k_3 + k_4)}\right\}^{1/2}$$

Hence, under these conditions, that is, at very low concentrations of the solute, the yield is directly proportional to the solute concentration and increases with decrease in the dose rate.

At some particular value of the solute concentration, which will be determined by the relative values of k_1 and $(k_3 + k_4)$, the yield will commence to depend on the solute concentration. In general, extremely reactive solutes will exhibit case (a) kinetics to lower concentrations than do less reactive solutes. It is also evident that radiations with high linear ion density, which tend to increase the $(k_3 + k_4)n$ term, will lead to change from case (a) to case (b) at higher solute concentrations than radiations with small linear ion density.

It is apparent from the preceding review that considerable work has been done on various radiation induced chemical reactions in aqueous solution. However, to obtain a clearer insight into the fundamental chemistry of such reactions there seemed to be a real need for an intensive and systematic study of one such reaction, giving attention, in particular, to the several variables that might influence the kinetics of reaction. These variables include solute concentration, pH, intensity and temperature under conditions of both aeration and deaeration of the solution. Owing to its importance as a chemical dosimeter, the reaction involving the radiation induced oxidation of ferrous sulfate was chosen as an appropriate subject for such an investigation. Specifically, the γ-ray induced oxidation of aqueous ferrous sulfate solution was studied, with the results given in subsequent sections of this thesis.

EXPERIMENTAL

The general techniques used throughout this study, such as preparation of water and aqueous solutions, analytical and irradiation procedures, will be described together since they are common to the entire investigation. Specific techniques, such as preparation of airfree solutions and gas analysis, will be fully described in Part B.

(a) Glass-Ware

All the glass-ware used in this study was thoroughly cleaned by the following procedure. It was allowed to stand in fresh cleaning solution over-night, then thoroughly washed with tap water, rinsed several times with distilled water, steamed out for about an hour and then rinsed three times with triple distilled water, the preparation of which is described below. This procedure was found to eliminate irreproducible results which were observed in the absence of such a rigid cleaning procedure.

(b) Preparation of Water and Solutions

It was found that reproducible results were obtained with distilled water (from a commercial still) which had been successively distilled from alkaline permanganate and then from an alkaline suspension of manganous hydroxide in a conventional all-glass pyrex still. The distillation was performed in a stream of nitrogen from a commercial cylinder. This treatment appeared to rid the water of any dissolved organic impurities and also of free chlorine.

Reagent special grade ferrous ammonium sulphate, $FeSO_4$-$(NH_4)_2SO_4 \cdot 6H_2O$, (Baker and Adamson) and C.P. reagent sulfuric acid, specific gravity = 1.84, (Nichols Chemical Co.) were used in the preparation of the solutions. The ferric ammonium sulfate used was reagent grade (Baker and Adamson) and was recrystallized once.

Stock solutions were prepared by dissolving a weighed amount of the salt in the purified water containing sulfuric acid, usually 0.8 N in sulfuric acid, and made to a known volume in a volumetric flask. Acidification with sulfuric acid was necessary to prevent spontaneous oxidation of the ferrous solutions, and with ferric solutions to prevent hydrolysis. Solutions of ferrous ion prepared in this way were found to be stable for several weeks; however, stock solutions were never used longer than about two weeks.

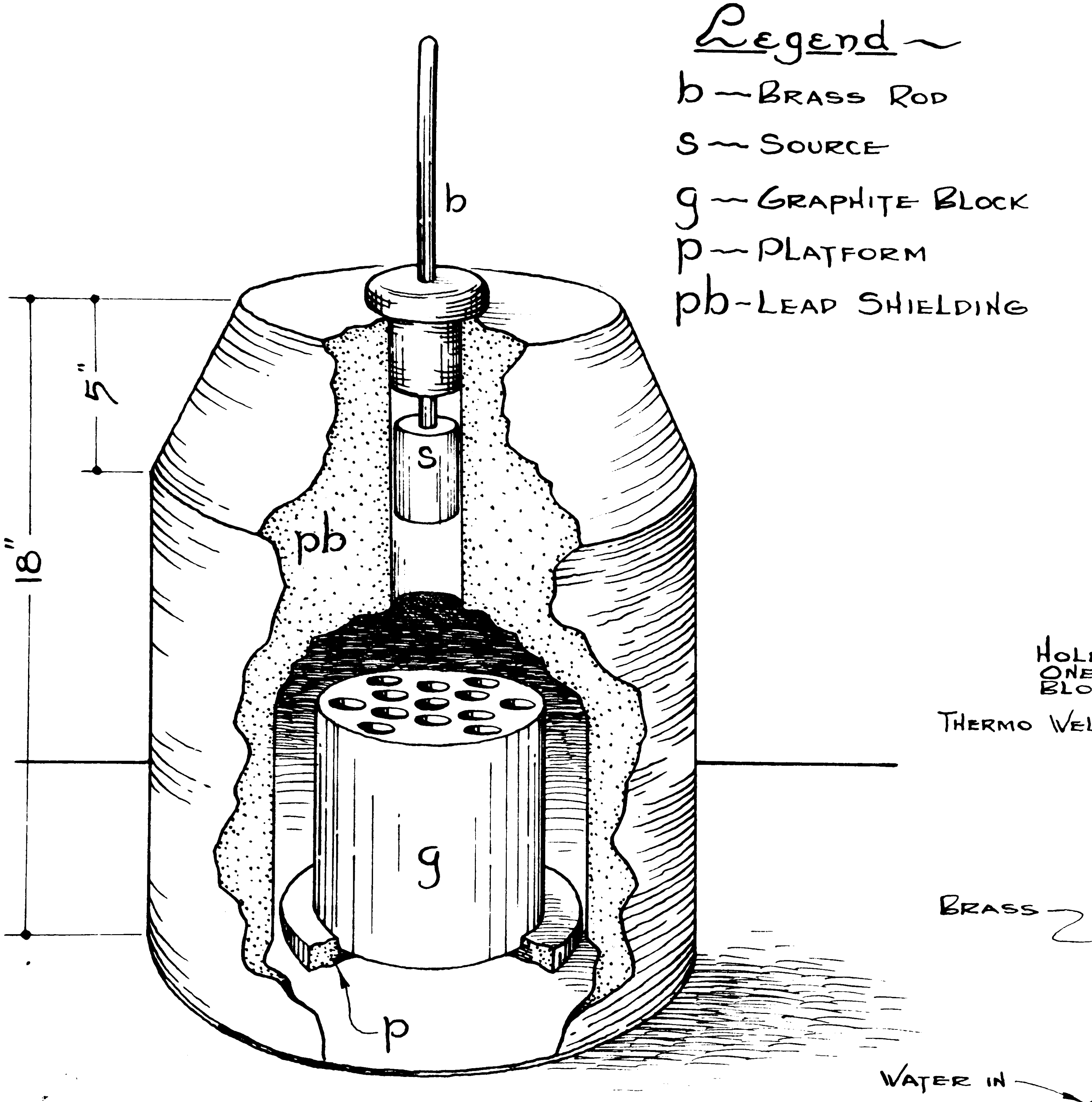
(c) Irradiation Method

In the early experiments the solutions were irradiated with the γ-rays from a 2 gm. radium source, and in later experiments with the γ-rays from an approximately 2 curie Co^{60} source. Interchange of these sources had no effect on the results. All experiments with the Co^{60} source have been corrected for radioactive decay, using a half-life of 5.0 years.

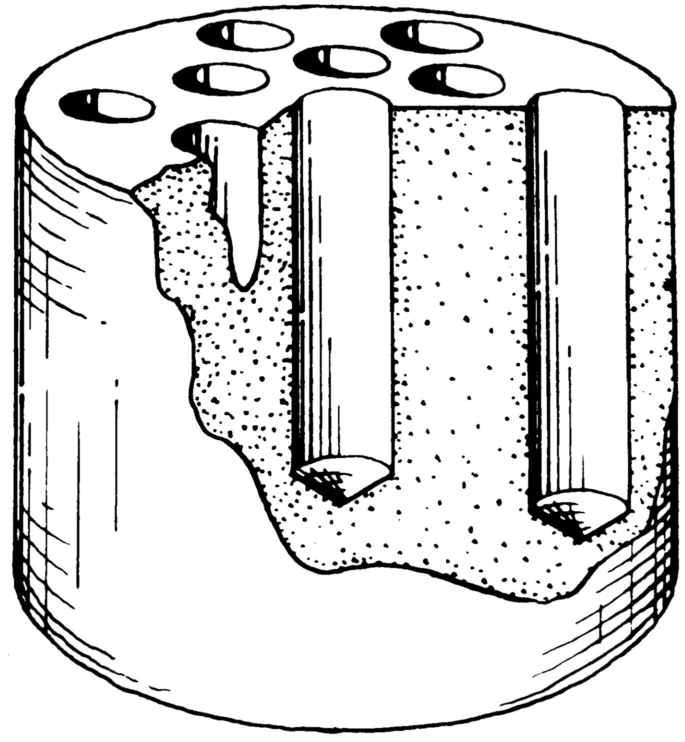
The radium preparation consisted of two 1 gm. sources (length 5/8", diameter 1/2") contained in a sealed source holder to prevent leakage of radon. The γ-rays from this source were effectively filtered through 0.5 mm. of platinum. The source was placed inside an aluminum capsule to which a long brass rod was attached for handling purposes. An identical aluminum capsule was used to contain the cobalt source. The cobalt source was prepared by neutron irradiation of commercially pure metallic cobalt (length 1/2", diameter 3/8") in the NRX nuclear reactor.

The irradiations were performed in a lead castle designed by Dr. T. J. Hardwick which allowed manipulation of the source without any danger of exposure to the operator. A cut-away section of the castle is shown in Figure 1. The castle contained a graphite block (height 4 1/2", diameter 4 1/2") which was machined to fit accurately the grooved platform inside the lead castle (see Figure 1). This ensured that the graphite block could be placed in a reproducible position. The lead castle was fitted with a removal lead door mounted on roller bearings. This arrangement allowed the easy removal of the graphite block. The graphite irradiation block was designed to accommodate the source in the central position surrounded by twelve sample positions disposed in two concentric rings, six positions per ring. With this arrangement a symmetrical distribution of the samples about the source was obtained and consequently the same geometry was maintained.

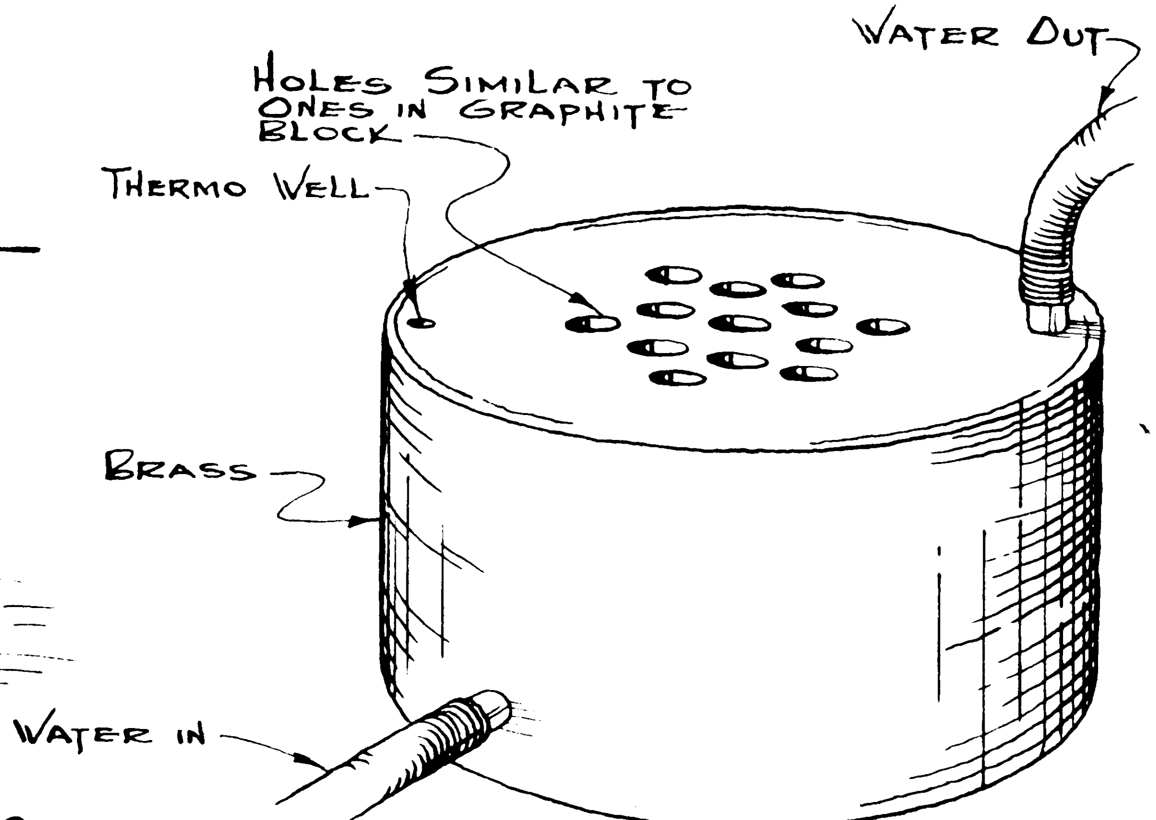
The solutions, usually 5 ml., were irradiated in pyrex tubes 1 mm. thick and 13 mm. internal diameter. The irradiation tubes were made to fit snugly into the positions in the graphite block. The steps involved in an actual irradiation were as follows: (i) the source was retracted into the heavily shielded upper portion of the castle and secured with a cotter pin; (ii) the lead door was swung open and the graphite block carefully placed in the grooved platform; (iii) the lead door was closed and the source lowered



— IRRADIATION APPARATUS —



Detail of Graphite Block



Constant Temperature Irradiation Device

FIGURE 7

into the graphite block. Control experiments, using the ferrous sulfate system as a chemical dosimeter, showed that the source could be placed in a reproducible position.

To study the effect of temperature on the oxidation of Fe^{+2} ion, a special irradiation container was constructed. It consisted of a hollow flat cylinder of brass (thermally insulated) through which water, from a constant temperature circulating bath, could be circulated. The disposition of source and irradiation positions were the same as with the graphite irradiation block (see Figure 1).

(d) Analytical Methods

The amount of oxidation at any time was determined by analysis for unreacted ferrous ion. The ferrous ion was determined colorimetrically by the o-phenanthroline method (71). Prior to each analysis a blank determination was made with the reagents. The procedure described below was followed, with the exception that 0.8 N sulfuric acid was added in place of the ferrous sulfate solution.

To an aliquot of the sample in a colorimeter tube, one drop of a 1% aqueous o-phenanthroline solution was added and sufficient 2 N sodium acetate to buffer the solution at pH 3. This was then diluted to 10 ml. with distilled water. The color of the ferrous o-phenanthroline complex reaches maximum intensity instantaneously and is stable for long periods of time in the presence of acetate buffer. The color intensity of the resulting solution was measured with a Klett-Summerson photoelectric colorimeter equipped with a green filter ($\lambda \sim 540$ mμ). The amount of ferrous ion in the sample was then obtained from a calibration curve. The colorimeter was calibrated on several different occasions with solutions of known ferrous ion concentration. Solutions of known ferrous ion concentration were prepared by dissolving accurately weighed amounts of the ferrous ammonium sulfate salt in 0.8 N sulfuric acid. Duplicate calibrations checked to within ± 1.0%. Data for a typical calibration are given in Table I.

The ferric o-phenanthroline complex was found to absorb only slightly at the wave-length used and in general a correction was not applied. However, in the presence of a large amount of ferric ion, eg., when ferric ion was actually added to the solution, it was necessary to correct for the absorption due to this complex. This correction was made by adding known amounts of ferric ion to the ferrous solution and the ferrous ion determined by the above procedure.

When it was necessary to analyze for ferric ion this was quantitatively reduced with hydroxylamine hydrochloride in aqueous hydrochloric acid (72). The ferrous ion was then determined by the o-phenanthroline method.

In some cases it was necessary to analyze for hydrogen peroxide in the irradiated solution. In the absence of ferrous ion, hydrogen peroxide was determined by adding an aliquot to a known excess of acidified ferrous solution and heating to about 70°C for two minutes. The solution was then cooled and the excess ferrous

TABLE 1

CALIBRATION OF COLORIMETER

(o-phenanthroline = 1%)
(sodium acetate = 2.0 N)

Fe^{+2} Concentration micromoles/liter	Colorimeter Reading
25	10
50	21
50*	22
100	42.5
100*	43
150	65
200	84
200*	85

* A new solution

ion determined by the o-phenanthroline method. The amount of hydrogen peroxide was calculated from the known stoichiometry for the reaction between ferrous ion and hydrogen peroxide, i.e., one mole of hydrogen peroxide oxidizes two moles of ferrous ion.

(e) Dosimetry

For the comparison of yields under various experimental conditions, it was advantageous to know the amount of energy that was actually absorbed by the solution. The most common method for determining the amount of energy absorbed from a γ-ray source has been to measure the saturation ion current in a suitable air-filled ionization chamber, converting this value to energy absorption in the aqueous solution. Such a method as this must be used since it is difficult to obtain saturation ion currents in a water-filled ionization chamber.

The unit of dose internationally employed for X- and γ-rays is the roentgen. This is defined as the quantity of X- or γ-radiation such that the associated corpuscular emission per 0.001293 gm. of air produces, in air, ions carrying 1 e.s.u. of quantity of electricity of either sign. This corresponds to the formation of 2.08×10^9 ion pairs per cc. of air at N.T.P., which involves an energy dissipation of 83 ergs per gm. of air. The latter figure is based on 32.5 ev as the mean energy required to form an ion pair in air. Since the roentgen is defined only for standard air, it does not always represent for different radiations the same energy dissipation in water. Hence, it is essential to convert a dose in roentgens into energy dissipation in water. This conversion is readily obtained from a knowledge of the ratio of the energy dissipation per unit volume in water and in air for the particular radiation.

Since the mass absorption coefficients for water and air are the same, then to a first approximation, the energy absorption per unit volume in the air ionization chamber, which is obtained from the ion current measurement, may be multiplied by the ratio of the densities of water and air to obtain the energy absorption per unit volume of water. This method assumes that the amount of energy required to form an ion pair in water is the same as for air, namely 32.5 ev. The accuracy of this method depends largely on the geometry of the irradiation cell. If the cell is too large there will be considerable absorption in the water and if it is too small an appreciable amount of the energy absorption will be due to secondary electrons from the cell walls, which are commonly of pyrex glass.

At the time that this investigation was started, Dr. N. Miller had just completed a critical study of the applicability of the ferrous sulfate system as a chemical dosimeter. His method was based on the Bragg-Gray cavity principle. According to this principle, it is only necessary to use a water wall ionization chamber, the linear dimensions of which are small compared with the range of of the secondary electrons in air, to obtain the energy absorption in the water. Consequently, the ionization per unit volume of air in the chamber will be the same as the ionization that would be observed in a small cavity in a large body of water. Polystyrene was found to meet the requirements of a water-equivalent wall material for γ-radiation. Thus, with a polystyrene ion chamber and irradiation cell of identical geometry, the number of ferrous ions oxidized was determined for a given energy absorbed in the solution. The value obtained by Miller for aerated ferrous sulfate solutions was 6.7 ferrous ions oxidized per 32.5 ev absorbed.

In this study the amount of energy absorbed by the solutions was determined with the ferrous sulfate chemical dosimeter, using the above value for the oxidation yield of ferrous ion in aerated solution.

RESULTS

(A) AERATED SOLUTION

Aerated solutions are those with which special precautions were not taken to remove dissolved air; that is, they contained the saturation concentration of air at the laboratory temperature (~23°C). Hence, the solutions contained the following approximate amounts of dissolved gases:

$$O_2 \simeq 3 \times 10^{-4} \text{ M}$$
$$N_2 \simeq 6 \times 10^{-4} \text{ M}$$

The aerated solutions were irradiated in pyrex test tubes stoppered with clean corks, thus an atmosphere of air was always maintained over the solutions. Unless otherwise stated, the solutions were made 0.8 N in sulfuric acid.

Effect of Fe^{+2} Ion Concentration on Yield in 0.8 N H_2SO_4

The variation of the initial Fe^{+2} ion oxidation yield was studied as a function of the initial Fe^{+2} ion concentration from 1×10^{-2} M to 7.4×10^{-6} M, in 0.8 N H_2SO_4 solutions. For each initial Fe^{+2} ion concentration studied an oxidation-energy absorbed curve was obtained, usually to complete oxidation. The results obtained are recorded in Tables II, III, IV, V and shown graphically in Figures II, III, IV, V, VI, VII, VIII.

It was found that between 1×10^{-2} M and 1×10^{-4} M Fe^{+2} ion concentration, the number of Fe^{+2} ions oxidized was a linear function of the energy absorbed to 100% oxidation. This linearity

TABLE II

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 1.0 \times 10^{-2}$ M			$(Fe^{+2}) = 1.0 \times 10^{-3}$ M		
Dose Rate ev/Hr/ml	Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml	Dose Rate ev/Hr/ml	Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml
$8.6\text{x}10^{16}$	$14.1\text{x}10^{17}$	$28.2\text{x}10^{16}$	$8.6\text{x}10^{16}$	$2.5\text{x}10^{17}$	$6.0\text{x}10^{16}$
	40.0	78.2		5.1	9.5
	60.6	119.2		5.2	10.6
$3.2\text{x}10^{16}$	$7.3\text{x}10^{17}$	$14.6\text{x}10^{16}$		14.7	30.4
	22.5	46.0		19.2	40.0
	29.2	58.0		22.0	45.0
				24.2	50.1
				39.6	60.2
			$3.2\text{x}10^{16}$	1.67	4.38
				6.91	14.0
				8.25	16.6
				14.1	29.0
				29.2	60.2

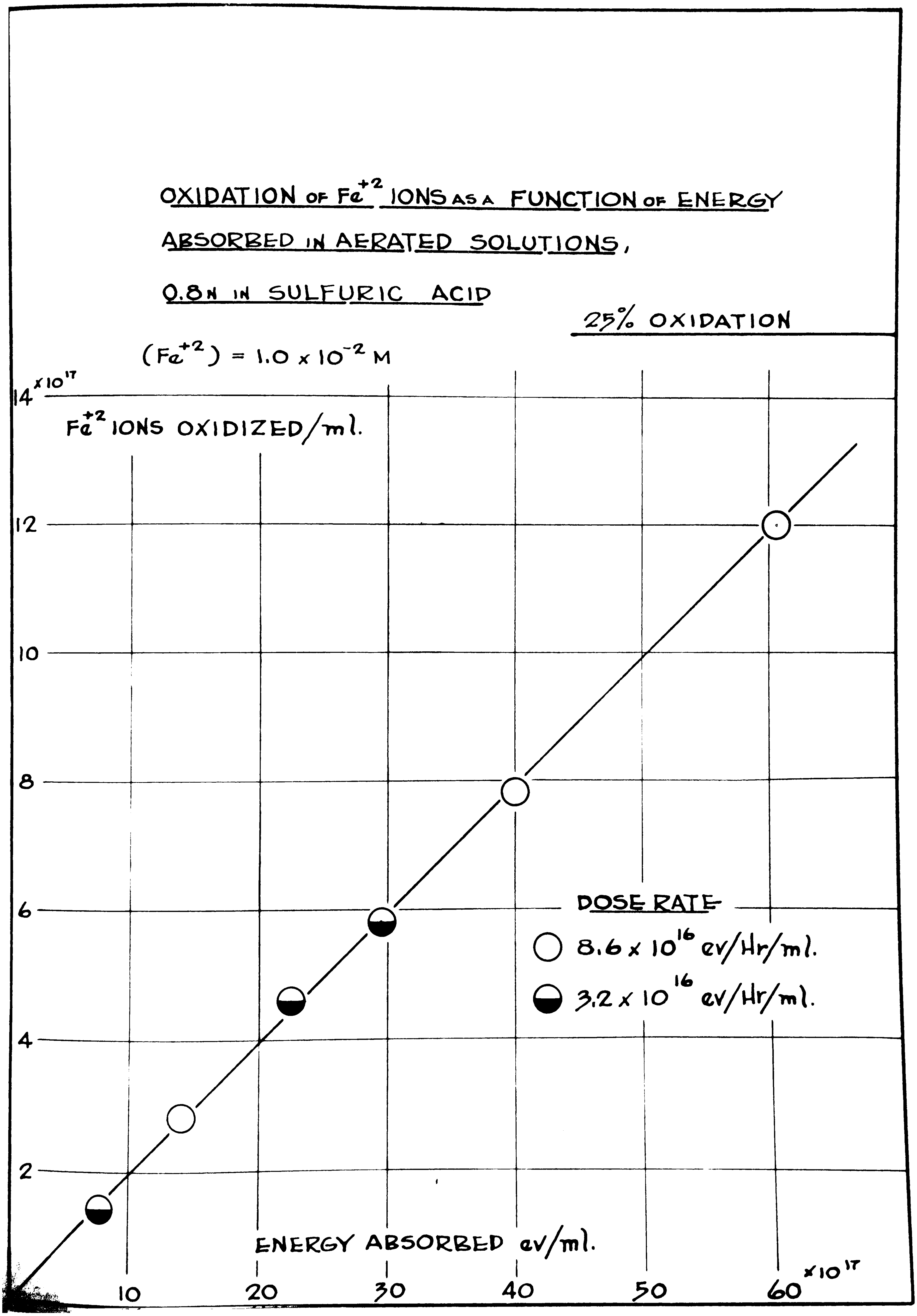

OXIDATION OF Fe+2 IONS AS A FUNCTION OF ENERGY
ABSORBED IN AERATED SOLUTIONS,
0.8N IN SULFURIC ACID
25% OXIDATION
(Fe+2) = 1.0 x 10-2 M
14 x10^17
Fe+2 IONS OXIDIZED/ml.
12
10
8
6
4
2
DOSE RATE
○ 8.6 x 10^16 ev/Hr/ml.
◒ 3.2 x 10^16 ev/Hr/ml.
ENERGY ABSORBED ev/ml.
10
20
30
40
50
60 x10^17

FIGURE II

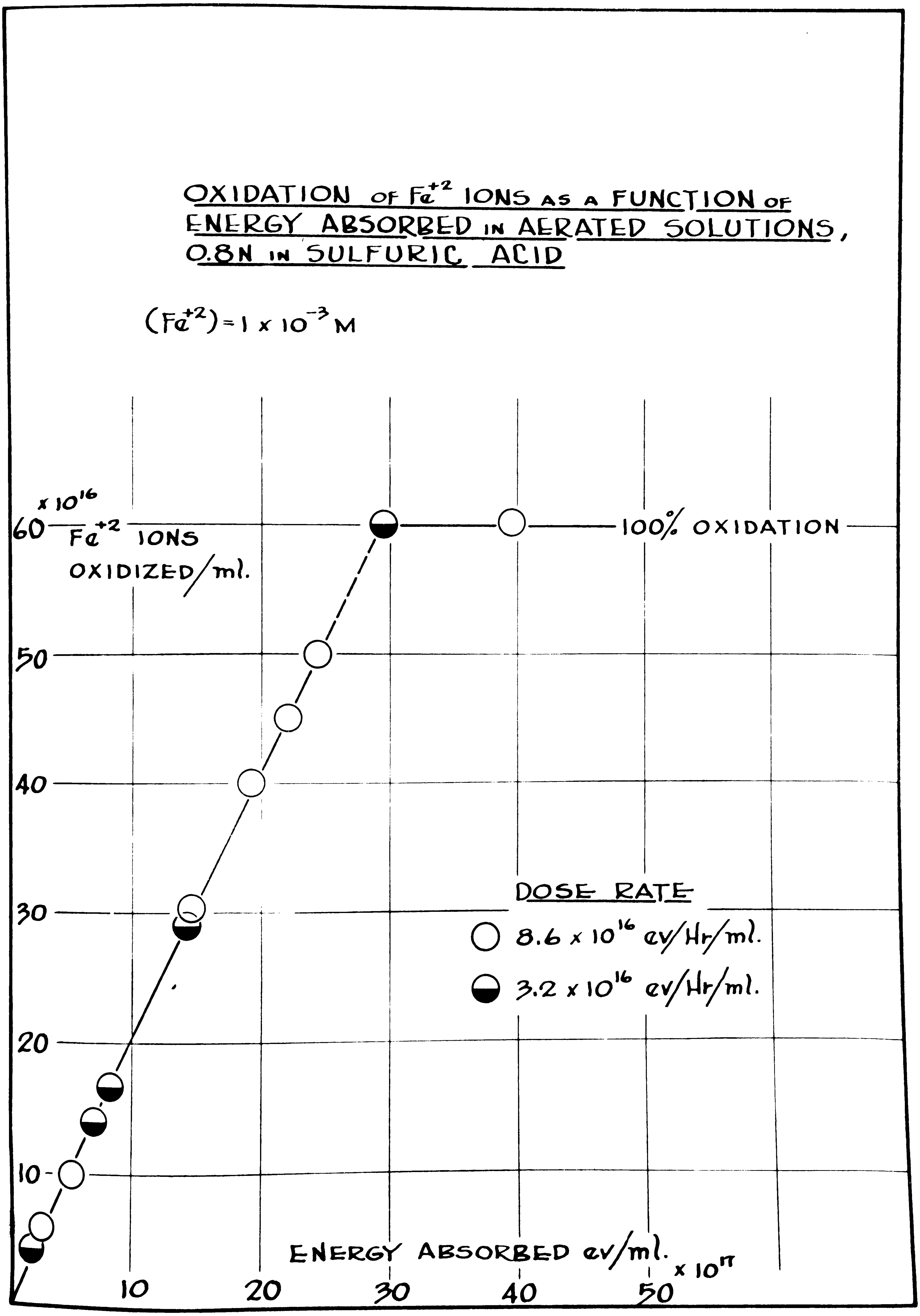

OXIDATION OF Fe^{+2} IONS AS A FUNCTION OF ENERGY ABSORBED IN AERATED SOLUTIONS, 0.8N IN SULFURIC ACID
$(Fe^{+2}) = 1 \times 10^{-3}$ M
$\times 10^{16}$
Fe^{+2} IONS OXIDIZED/ml.
60
50
40
30
20
10
100% OXIDATION
DOSE RATE
○ 8.6×10^{16} ev/Hr/ml.
◒ 3.2×10^{16} ev/Hr/ml.
ENERGY ABSORBED ev/ml.
$\times 10^{17}$
10
20
30
40
50

FIGURE III

TABLE III

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 2.5 \times 10^{-4}$ M		$(Fe^{+2}) = 1.0 \times 10^{-4}$ M		
Dose Rate = 1.0×10^{17} ev/Hr/ml				
Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml	Dose Rate ev/Hr/ml	Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
5.1×10^{16}	9.65×10^{15}	8.6×10^{16}	4.3×10^{16}	7.0×10^{15}
10.2	20.7		8.6	17.0
20.4	40.0		12.9	26.5
30.6	62.1		17.3	35.0
40.8	81.5		21.6	43.6
51.0	102		25.9	52.3
56.1	115		28.4	56.5
			34.6	60.2
			43.3	60.2
		3.2×10^{16}	1.6	3.5
			3.2	6.9
			6.9	14.0
			14.3	30.4

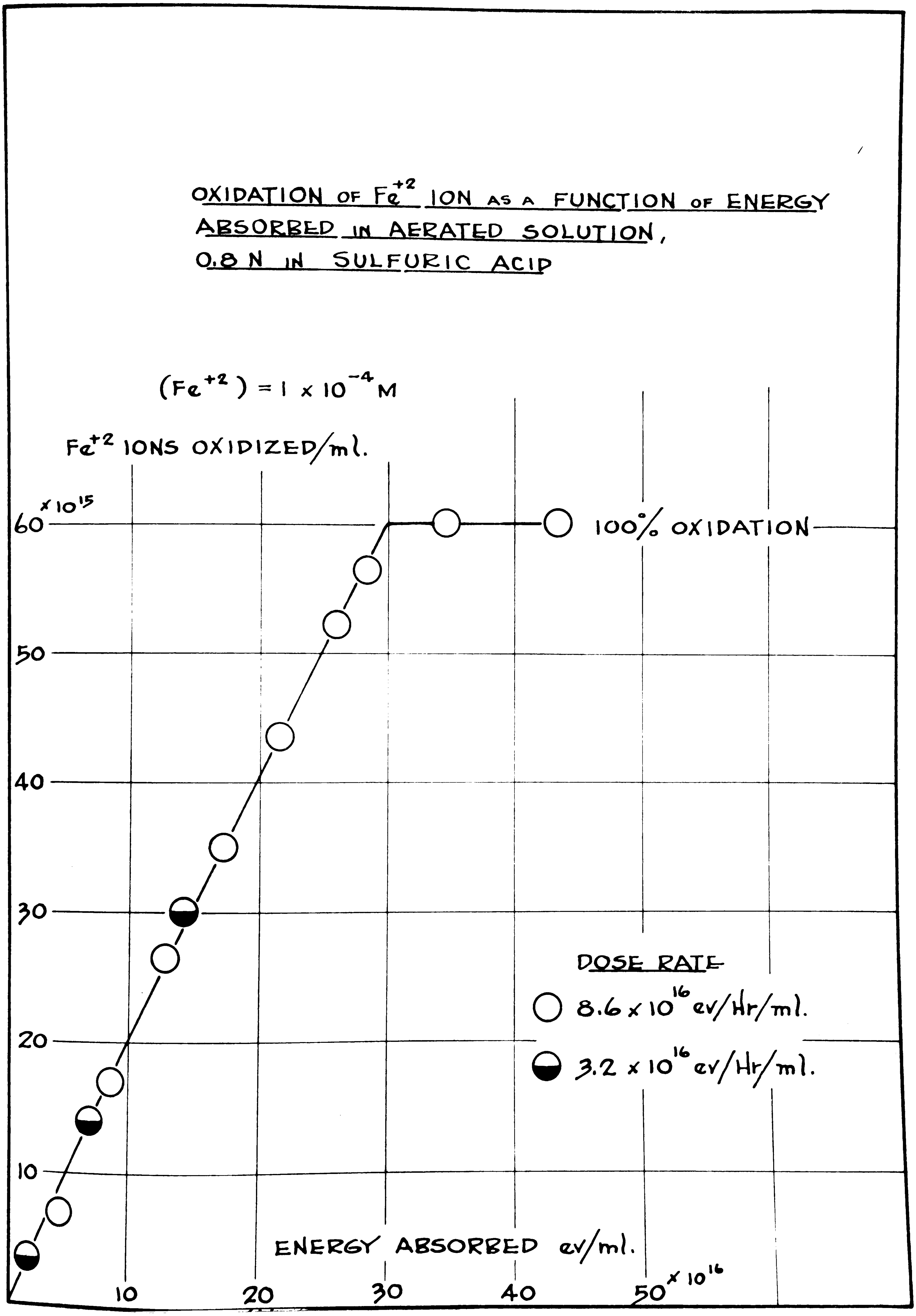

OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED IN AERATED SOLUTION, 0.8 N IN SULFURIC ACID
$(Fe^{+2}) = 1 \times 10^{-4}$ M
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
60
50
40
30
20
10
100% OXIDATION
DOSE RATE
○ 8.6×10^{16} ev/Hr/ml.
◒ 3.2×10^{16} ev/Hr/ml.
ENERGY ABSORBED ev/ml.
10
20
30
40
50
$\times 10^{16}$

FIGURE IV

also indicated that the yield, which is the slope at any point, is independent of the instantaneous Fe^{+2} ion concentration over a very wide range. In addition, the slopes of the curves shown in Figures II, III and IV were all found to be the same, that is, the oxidation yield is independent of the initial Fe^{+2} ion concentration between 1×10^{-2} M and 1×10^{-4} M. It was also found that between these limits of Fe^{+2} ion concentration, the oxidation yield was independent of the intensity between 8.6×10^{16} and 3.2×10^{16} ev/hr./ml.

Below an initial Fe^{+2} ion concentration of 10^{-4} M it was observed that the initial oxidation yield decreased. The curves shown in Figures V, VI, VII and VIII show that the oxidation is a linear function of the energy absorbed to approximately 70%. Above 70% oxidation, however, the number of Fe^{+2} ions oxidized appeared to decrease exponentially with the energy absorbed. Hence, the oxidation appears to change from zero order to approximately first order kinetics with respect to the Fe^{+2} ion concentration.

The initial oxidation yields, obtained from the initial slopes of the oxidation-energy absorbed curves for the complete range studied, 1×10^{-2} M to 7.4×10^{-6} M, are recorded as a function of the initial Fe^{+2} ion concentration in Table VI and shown graphically as a semi-log plot in Figure IX. This figure clearly shows that the initial oxidation yield is 20.2 ± 0.4 Fe^{+2} ions oxidized/100 ev, independent of the Fe^{+2} ion concentration between 1×10^{-2} and 1×10^{-4} M. Below the latter concentration the initial yield decreases gradually with decrease in the Fe^{+2} ion concentration. There appears to be a tendency, at the lowest concentration studied, for the initial oxidation yield again to become independent of the initial Fe^{+2} ion concentration. Unfortunately, the analytical method would not permit extension to lower concentrations of Fe^{+2} ion.

TABLE IV

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Aerated Solution, 0.8 N in Sulfuric Acid

Dose Rate = 8.6×10^{16} ev/Hr/ml

$(Fe^{+2}) = 7.3 \times 10^{-5}$ M		$(Fe^{+2}) = 5.0 \times 10^{-5}$ M	
Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml	Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml
4.3×10^{16}	9.3×10^{15}	2.1×10^{16}	4.3×10^{15}
8.6	16.6	4.3	9.0
12.9	25.6	6.3	12.5
15.0	28.7	7.9	15.2
17.2	31.8	9.0	17.5
19.3	35.6	10.8	20.5
21.5	38.0	12.9	24.5
		15.1	27.0
		17.3	28.7
		19.3	29.5

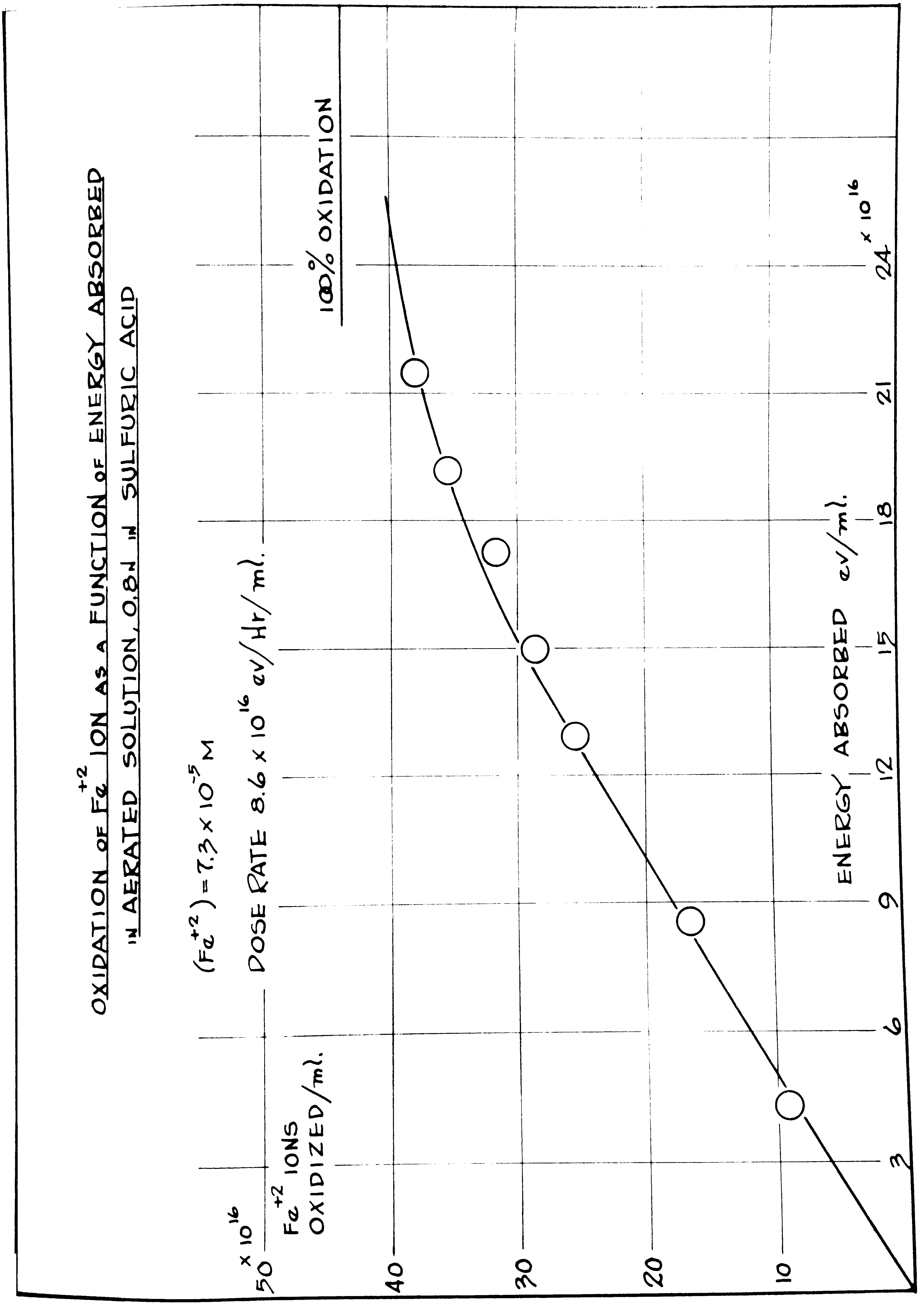

OXIDATION OF Fe+2 ION AS A FUNCTION OF ENERGY ABSORBED
IN AERATED SOLUTION, 0.8N IN SULFURIC ACID
(Fe+2) = 7.3 × 10-5 M
DOSE RATE 8.6 × 10^16 eV/Hr/ml.
100% OXIDATION
Fe+2 IONS OXIDIZED/ml.
× 10^16
50
40
30
20
10
ENERGY ABSORBED eV/ml.
3
6
9
12
15
18
21
24 × 10^16

FIGURE V

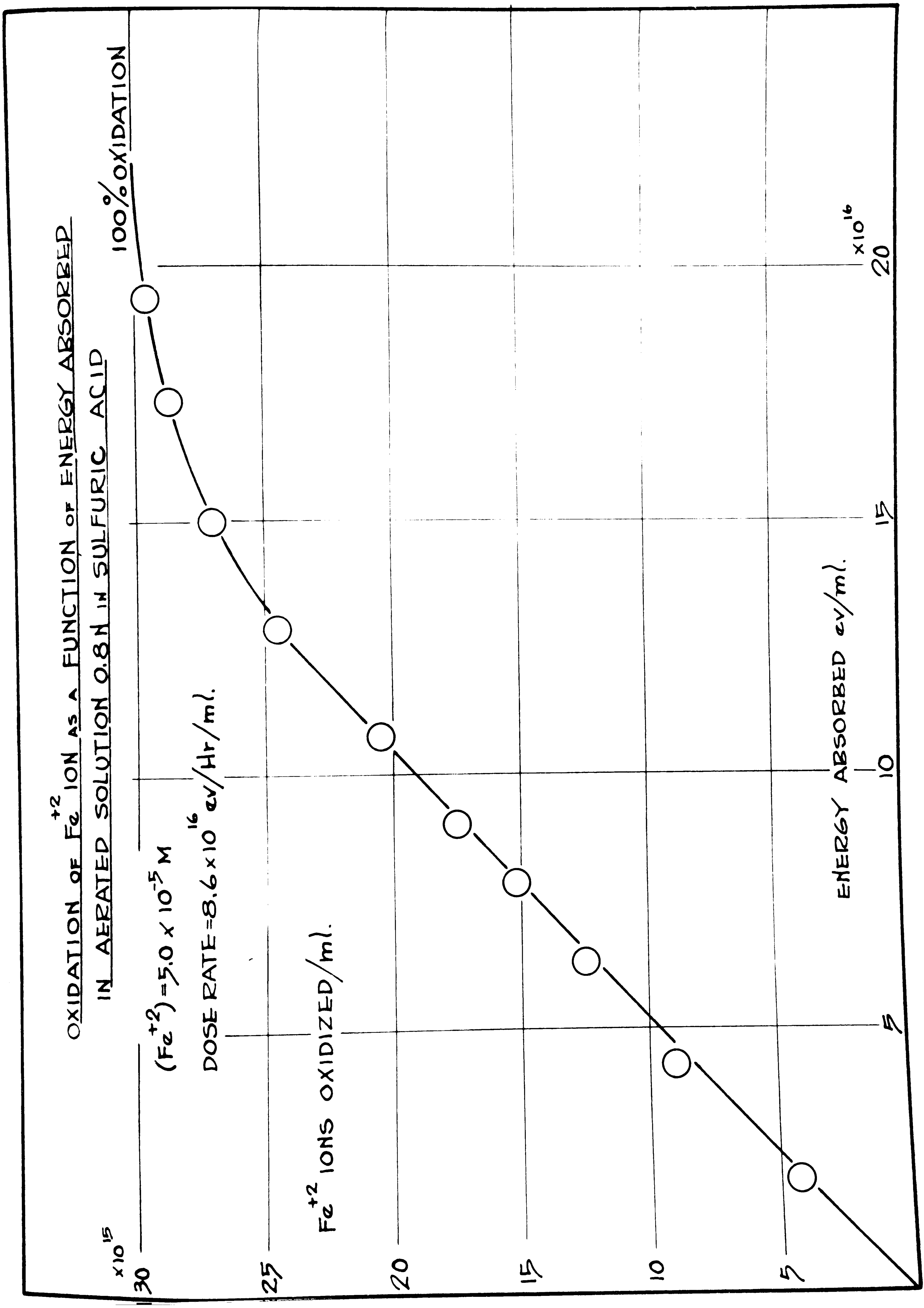

OXIDATION OF Fe+2 ION AS A FUNCTION OF ENERGY ABSORBED
IN AERATED SOLUTION 0.8N IN SULFURIC ACID
(Fe+2)=5.0 x 10-5 M
DOSE RATE=8.6x10 16 ev/Hr/ml.
Fe+2 IONS OXIDIZED/ml.
x10 15
30
25
20
15
10
5
ENERGY ABSORBED ev/ml.
x10 16
5
10
15
20
100% OXIDATION

FIGURE VI

TABLE V

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Aerated Solution, 0.8 N in Sulfuric Acid

Dose Rate = 8.6 x 10^{16} ev/Hr/ml

(Fe^{+2}) = 2.5 x 10^{-5} M		(Fe^{+2}) = 1.1 x 10^{-5} M	
Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml	Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml
2.2 x 10^{16}	3.95 x 10^{15}	1.0 x 10^{16}	1.30 x 10^{15}
4.5	7.20	2.2	2.33
6.8	11.2	3.3	3.75
8.6	12.9	4.4	5.15
10.7	13.9	6.4	5.94
		8.6	6.32

(Fe^{+2}) = 7.4 x 10^{-6} M	
Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml
7.2 x 10^{15}	6.91 x 10^{14}
14.3	15.9
21.5	22.1
28.7	29.0

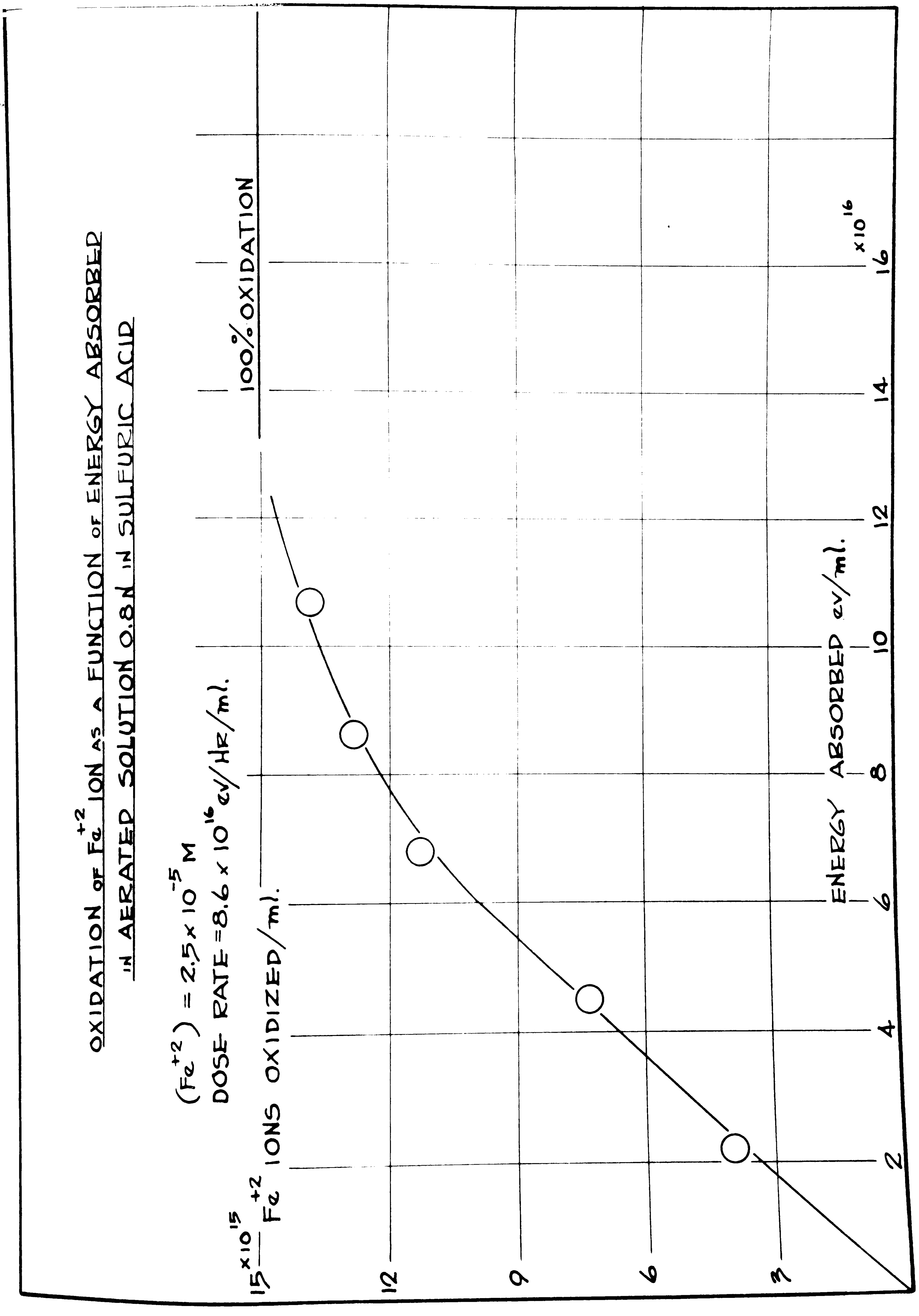

OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED
IN AERATED SOLUTION 0.8N IN SULFURIC ACID
$(Fe^{+2}) = 2.5 \times 10^{-5}$ M
DOSE RATE = 8.6×10^{16} eV/HR/ml.
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
15
12
9
6
3
100% OXIDATION
ENERGY ABSORBED eV/ml.
$\times 10^{16}$
2
4
6
8
10
12
14
16

FIGURE VII

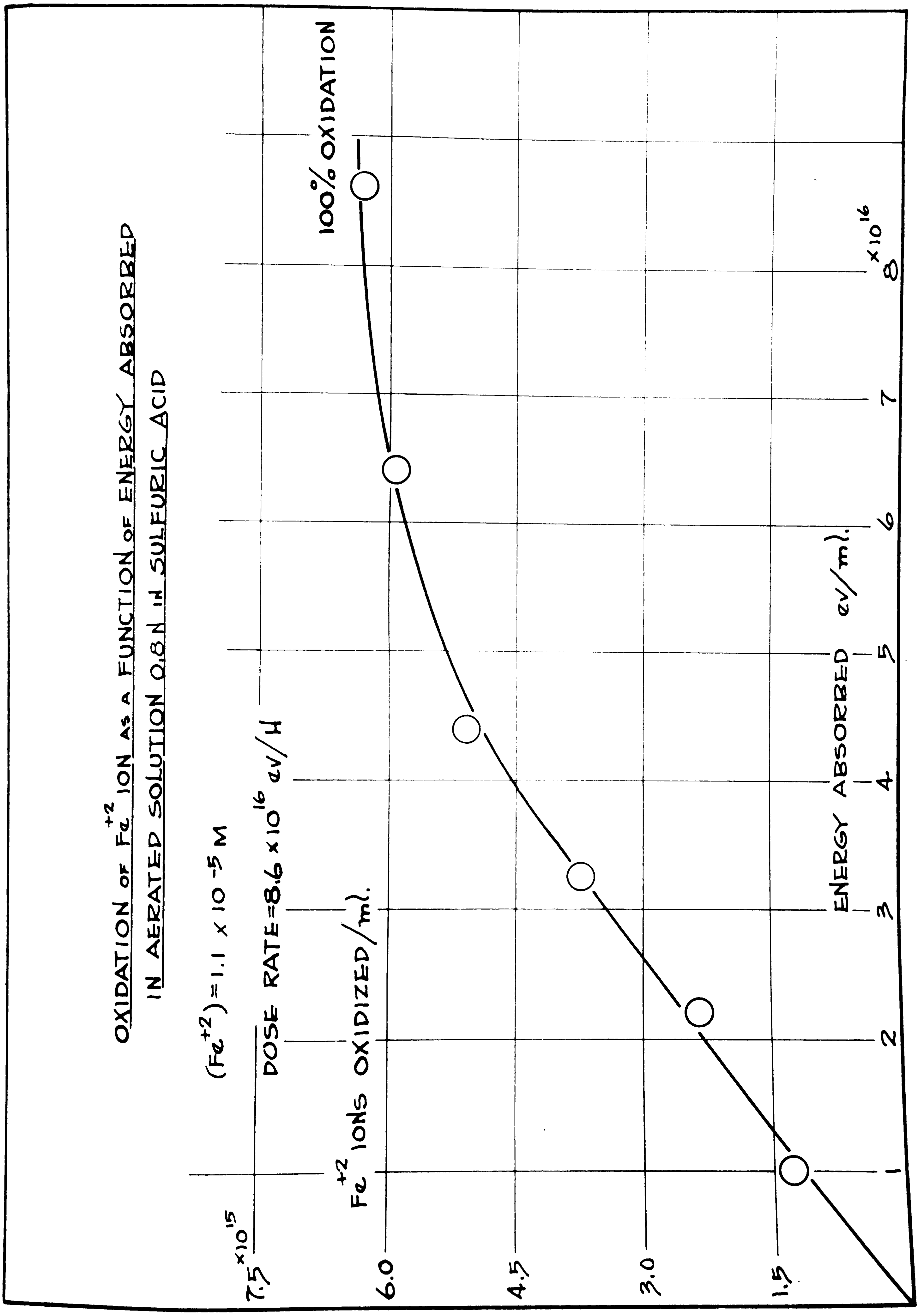

OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED
IN AERATED SOLUTION 0.8N IN SULFURIC ACID
$(Fe^{+2}) = 1.1 \times 10^{-5}$ M
DOSE RATE = 8.6×10^{16} ev/H
Fe^{+2} IONS OXIDIZED/ml.
$7.5^{\times 10^{15}}$
6.0
4.5
3.0
1.5
100% OXIDATION
ENERGY ABSORBED ev/ml.
1
2
3
4
5
6
7
$8^{\times 10^{16}}$

FIGURE VIII

TABLE VI

Initial Oxidation Yield as a Function of Initial Fe^{+2} Ion Concentration in Aerated 0.8 N Sulfuric Acid

Dose Rate = 8.6×10^{16} ev/Hr/ml

Initial (Fe^{+2}) moles/liter	Initial Oxidation Yield Fe^{+2} ions oxidized/100 ev
1.0×10^{-2}	20.1
1.0×10^{-3}	20.3
2.5×10^{-4}	20.2
1.0×10^{-4}	20.4
7.5×10^{-5}	19.8
5.0×10^{-5}	19.1
2.5×10^{-5}	16.7
1.1×10^{-5}	11.4
1.0×10^{-5}	11.2
7.4×10^{-6}	9.9

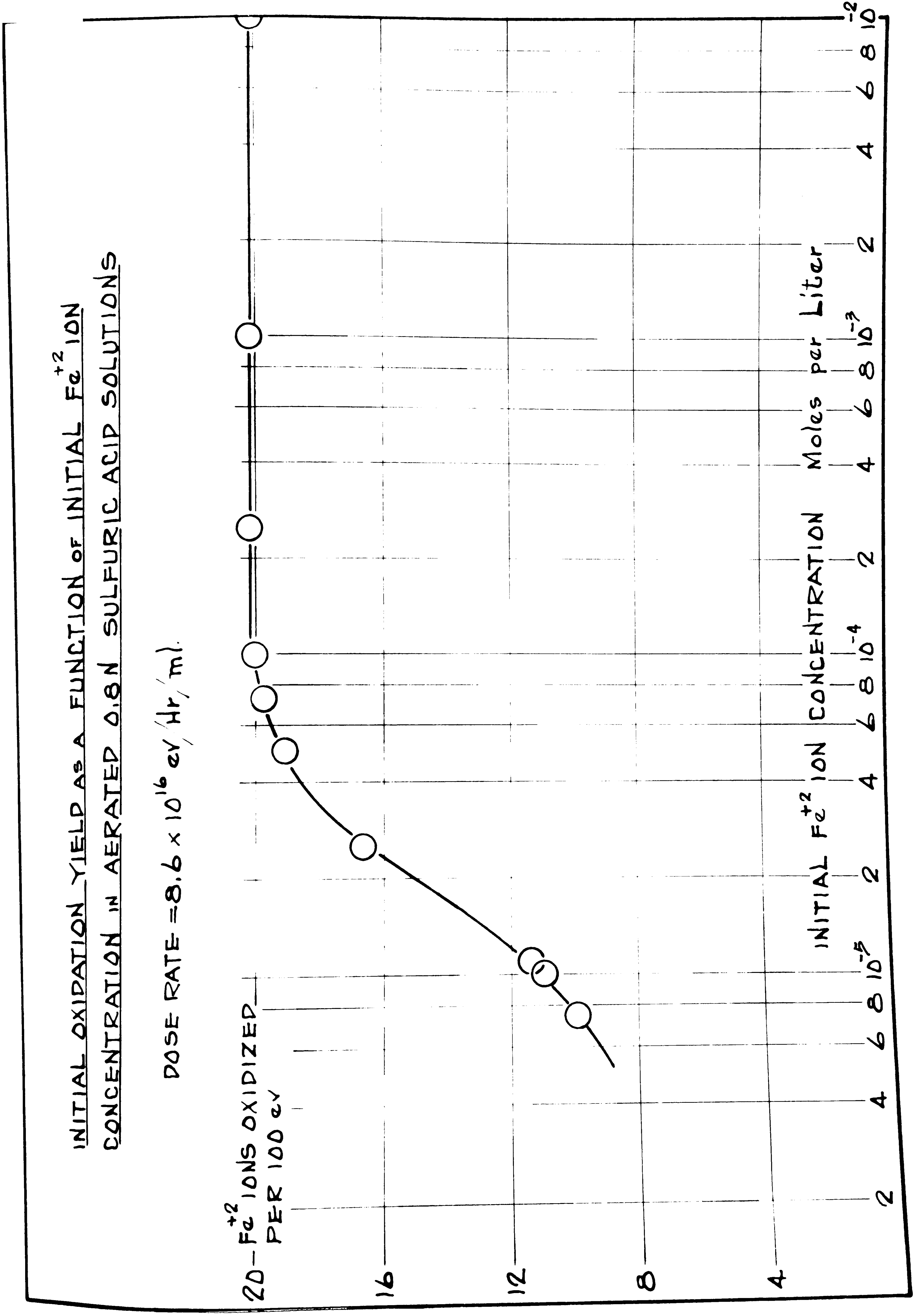

INITIAL OXIDATION YIELD AS A FUNCTION OF INITIAL Fe+2 ION
CONCENTRATION IN AERATED 0.8N SULFURIC ACID SOLUTIONS
DOSE RATE = 8.6 × 10^16 eV/Hr/ml.
Fe+2 IONS OXIDIZED PER 100 eV
20
16
12
8
4
INITIAL Fe+2 ION CONCENTRATION Moles per Liter
2
4
6
8
10^-5
2
4
6
8
10^-4
2
4
6
8
10^-3
2
4
6
8
10^-2

FIGURE IX

Formation of H_2O_2 in Aerated 0.8 N H_2SO_4 Solutions

The presence of oxygen dissolved in water is known to increase greatly the production of hydrogen peroxide under irradiation with X-rays. There was a concept prevalent about twenty years ago that the chemical action of ionizing radiations in aqueous solution could be attributed entirely to the production of H_2O_2. Fricke and Brownscombe had in fact found that the reduction of dichromate in acid solutions by X-rays could be accounted for completely by the production of H_2O_2 in the irradiated water.

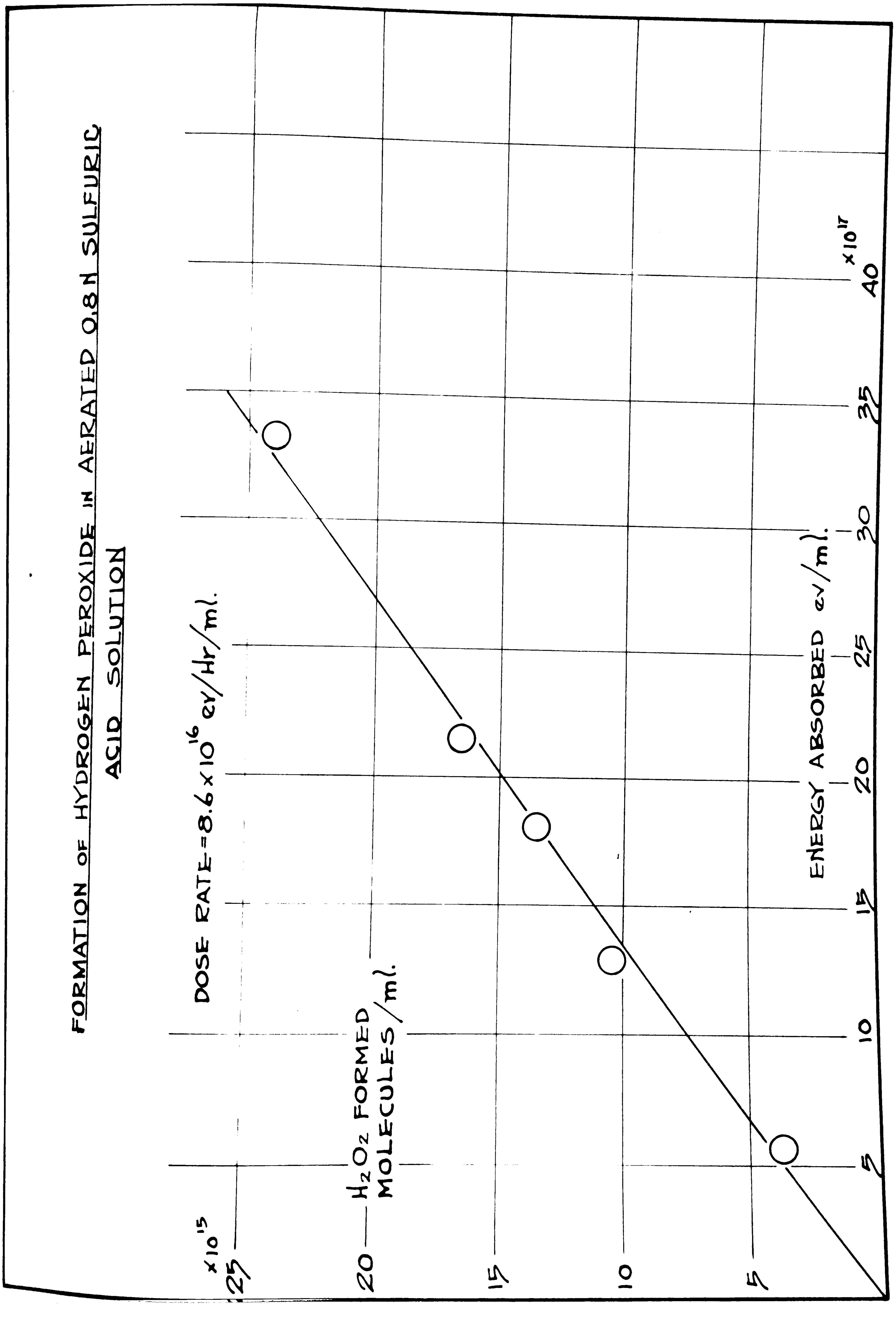
Since, in the present study, the Fe^{+2} ion solutions contained the saturation concentration of dissolved air, it appeared worthwhile to compare the production of H_2O_2 in 0.8 N H_2SO_4 with the oxidation of Fe^{+2} ion, under comparable experimental conditions. These results are given in Table VII and recorded graphically in Fig. X, from which it appears that the yield of H_2O_2, 0.7_5 molecules formed/100 ev, could only account for about 4% of the Fe^{+2} ion oxidation, in the region of concentration independence.

TABLE VII

Formation of H_2O_2 in Aerated 0.8 N H_2SO_4

Dose Rate = 8.6×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	H_2O_2 Formed molecules/ml
2.62×10^{17}	3.78×10^{15}
5.14	3.78
12.9	10.5
18.1	13.5
21.5	16.5
33.2	24.1



FORMATION OF HYDROGEN PEROXIDE IN AERATED 0.8 N SULFURIC ACID SOLUTION

Effect of $(NH_4)_2SO_4$ on the Oxidation of Fe^{+2} Ion in 0.8 N H_2SO_4

The effect of ammonium sulfate on the oxidation of Fe^{+2} ion in 0.8 N H_2SO_4 was investigated by a comparison of the oxidation yields obtained with ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, (Baker and Adamson) and ferrous sulfate, $FeSO_4 \cdot 7H_2O$, (Merck). Solutions of these solutes were prepared as previously described and irradiated under identical conditions. The results of this experiment are given in Table VIII from which it is evident that the oxidation of Fe^{+2} ion is independent of the $(NH_4)_2SO_4$ present in the ferrous ammonium sulfate.

TABLE VIII

Effect of $(NH_4)_2SO_4$ on the Oxidation of Fe^{+2} Ion in 0.8 N Sulfuric Acid

$(Fe^{+2}) = 1 \times 10^{-4}$ M

Dose Rate = 8.6×10^{16} ev/Hr/ml

$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$		$FeSO_4 \cdot 7H_2O$	
Energy Absorbed ev/ml	$\Delta\,(Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta\,(Fe^{+2})$ ions/ml
4.3×10^{16}	8.5×10^{15}	4.3×10^{16}	8.7×10^{15}
8.6	17.3	8.6	17.6
12.9	26.5	12.9	26.4
17.3	35.0	15.0	31.2
21.6	43.6	19.3	37.4
25.9	52.3	23.6	47.5
28.4	56.5	28.0	54.0
Oxidation Yield = 20.1 Fe^{+2} ions oxidized/100 ev.		Oxidation Yield = 20.1 Fe^{+2} ions oxidized/100 ev.	

Effect of Fe^{+3} Ion on Fe^{+2} Ion Oxidation in 0.8 N H_2SO_4

In the region of concentration independence, the previous results show that the oxidation of Fe^{+2} ion is a linear function of the energy absorbed to complete oxidation. This implies that the reaction product, Fe^{+3} ion, does not take part in the reaction, that is, there is no back reaction in which the Fe^{+3} ion is reduced to Fe^{+2} ion in 0.8 N H_2SO_4. It has been found that the addition of a tenfold excess of Fe^{+3} ion to the Fe^{+2} ion solution prior to the irradiation had no appreciable effect on the initial oxidation yield. The results are given in Table IX and Fig. XI. The dotted line in the figure indicates the course of the reaction in the absence of the tenfold excess of Fe^{+3} ion. Above 50% oxidation the oxidation was greatly retarded. In the analysis of these solutions corrections were made for the large amount of Fe^{+3} ion present, consequently, it is believed that the inhibition above 50% oxidation is a real effect.

It has also been found that solutions of Fe^{+3} ion (1×10^{-4} M) in aerated 0.8 N H_2SO_4 were not reduced to Fe^{+2} ion when irradiated with γ-rays with doses of the order of 2×10^{18} ev/ml. Furthermore, it was observed that irradiation of a 1×10^{-3} M Fe^{+3} ion solution with 2.0 Mev X-rays delivered at a dose rate several hundred times greater than that obtained from the γ-source, did not reduce Fe^{+3} ion in the presence of 0.8 N H_2SO_4. With both X- and γ-radiation, the irradiated Fe^{+3} solutions were found to contain appreciable amounts of H_2O_2.

TABLE IX

Effect of Fe^{+3} Ion on Fe^{+2} Ion Oxidation in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

$(Fe^{+3}) = 1.0 \times 10^{-3}$ M

Dose Rate = 8.6×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	Fe^{+2} Oxidized ions/ml
2.14×10^{16}	4.8×10^{15}
4.3	8.3
6.5	13.8
8.6	20.1
12.9	27.0
17.5	35.2
21.4	37.6
25.9	41.5
30.2	44.3
34.6	48.5
38.9	48.5
43.0	48.5

EFFECT OF Fe^{+3} ION ON OXIDATION OF Fe^{+2} ION IN AERATED SOLUTION, 0.8N IN SULFURIC ACID

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

$(Fe^{+3}) = 1.0 \times 10^{-3}$ M

DOSE RATE = 8.6×10^{16} ev/Hr/ml.

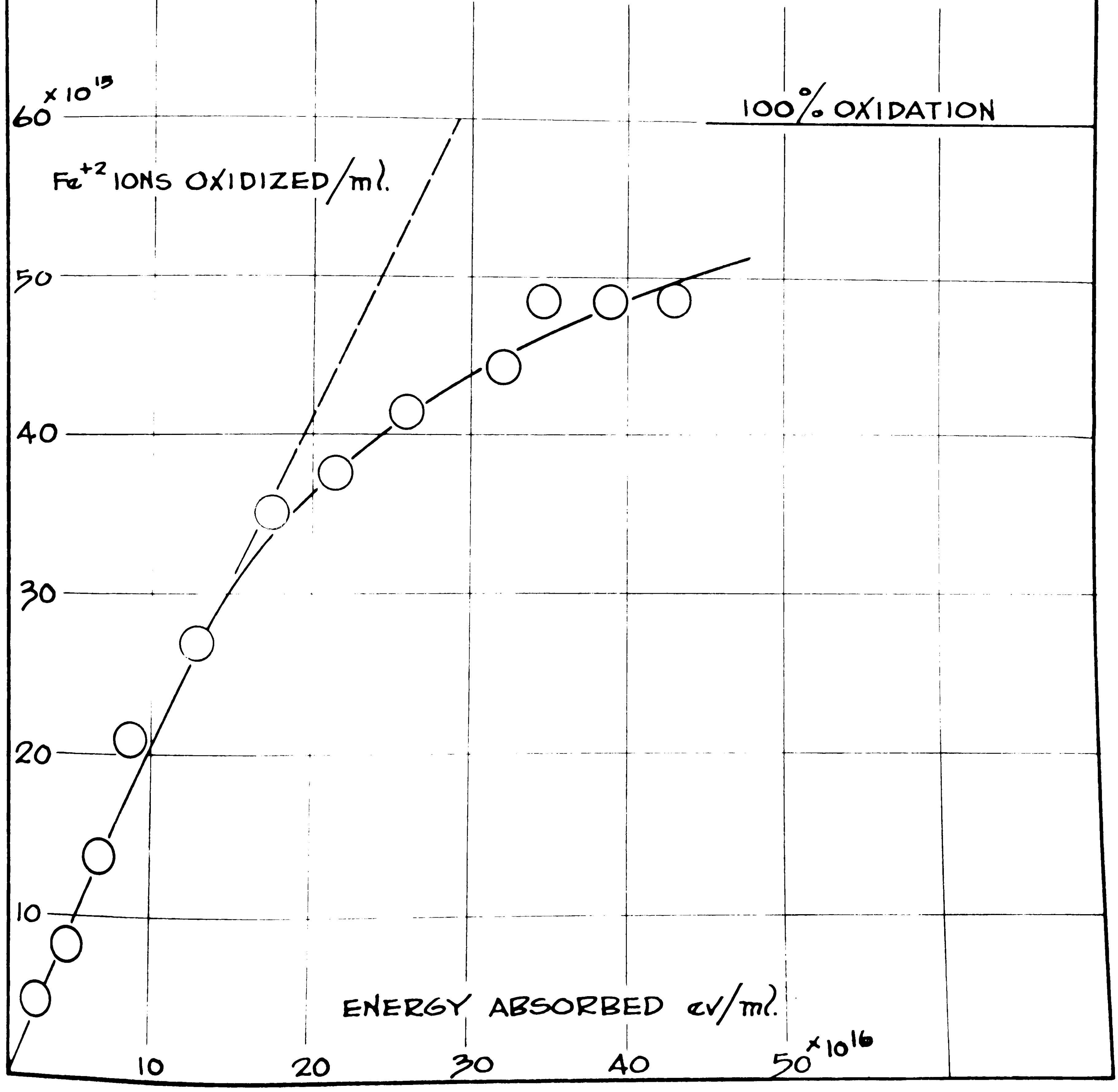


FIGURE XI

Effect of Temperature on Oxidation Yield in 0.8 N H_2SO_4

The early work of Fricke and Morse indicated that the oxidation of Fe^{+2} ions by X-radiation had a negligible temperature coefficient. Recently, Minder and Liechti have studied the effect of temperature between 4° and 54° and concluded that the oxidation yield was independent of temperature.

In the present investigation, the effect of temperature was studied by using the specially designed hollow brass cylinder which has been described under experimental technique (see Fig. I). Before studying the effect of temperature, it was ascertained that the source could be placed in a reproducible position in the brass block. The range of temperature studied was from 20° to 60°C. Prior to the irradiation of a solution it was pre-heated at the required temperature for 30 minutes. The results of these experiments, given in Table X, indicate a small positive temperature coefficient. Concentrations of Fe^{+2} ion of 2×10^{-4} M and 1×10^{-4} M gave the same temperature coefficient. Control experiments showed negligible oxidation during the time of these experiments.

TABLE X

Effect of Temperature on Oxidation Yield in Aerated 0.8 N Sulfuric Acid Solutions

$(Fe^{+2}) = 2.0 \times 10^{-4}$ M

Dose Rate = 3×10^{16} ev/Hr/ml

Temperature °C	1/T °K-1	Initial Oxidation Yield Fe^{+2} ions oxidized/100 ev
20	3.41×10^{-3}	20.2
40	3.19	22.4
59.5	3.01	24.4

Effect of Acid Concentration on Oxidation of Fe^{+2} Ion

A study of the effect of sulfuric acid concentration on the Fe^{+2} ion oxidation revealed that the initial yield decreased with decrease in acid concentration below 0.1 N H_2SO_4. Between 0.1 N and 0.8 N H_2SO_4 the yield was unchanged. This is in substantial agreement with the earlier work of Fricke. The effect of acid concentration was investigated at Fe^{+2} ion concentrations of 1×10^{-4} M and 2.2×10^{-4} M and the results were found to be identical. These are recorded in Tables XI and XII and Figs. XII and XIII. The dotted line in these figures shows the oxidation of Fe^{+2} ion in the presence of 0.8 N H_2SO_4. The results show that a decrease in the acid concentration decreases the initial slope of the oxidation-energy absorbed curve yet the curve is still linear initially. It is also apparent from these curves that the oxidation is not quantitative and appears to attain a steady value. It has also been found that the addition of 1.0 M Na_2SO_4 to a solution 0.001 N in H_2SO_4 had no effect on the oxidation, as shown in Table XIII and Fig. XIV. The solid line in this figure represents the results in the absence of sodium sulfate and the circles are the results in the presence of sodium sulfate.

The results for the effect of acid on the initial oxidation yield are summarized in Table XIV and Fig. XV. The initial oxidation yield was found to decrease by about 12% between 0.8 N and 0.01 N acid, and by about 36% between 0.8 N and 0.001 N acid. However, between 0.8 N and 0.1 N the initial oxidation yield was found to be unchanged.

TABLE XI

Effect of Sulfuric Acid Concentration on Oxidation of Fe^{+2} Ion in Aerated Solution

$(Fe^{+2}) = 2.2 \times 10^{-4}$ M

Dose Rate = 8.6×10^{16} ev/Hr/ml

$(H_2SO_4) = 1.0 \times 10^{-2}$ N		$(H_2SO_4) = 1.0 \times 10^{-3}$ N	
Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
5.1×10^{16}	9.5×10^{15}	12.6×10^{16}	15.9×10^{15}
10.2	18.6	21.2	26.9
20.4	37.4	35.7	44.8
30.6	55.3	40.8	50.5
40.4	75.5	51.0	61.5
51.0	92.5	59.2	69.0
61.2	110	71.4	72.1
71.4	121		
82.1	128		

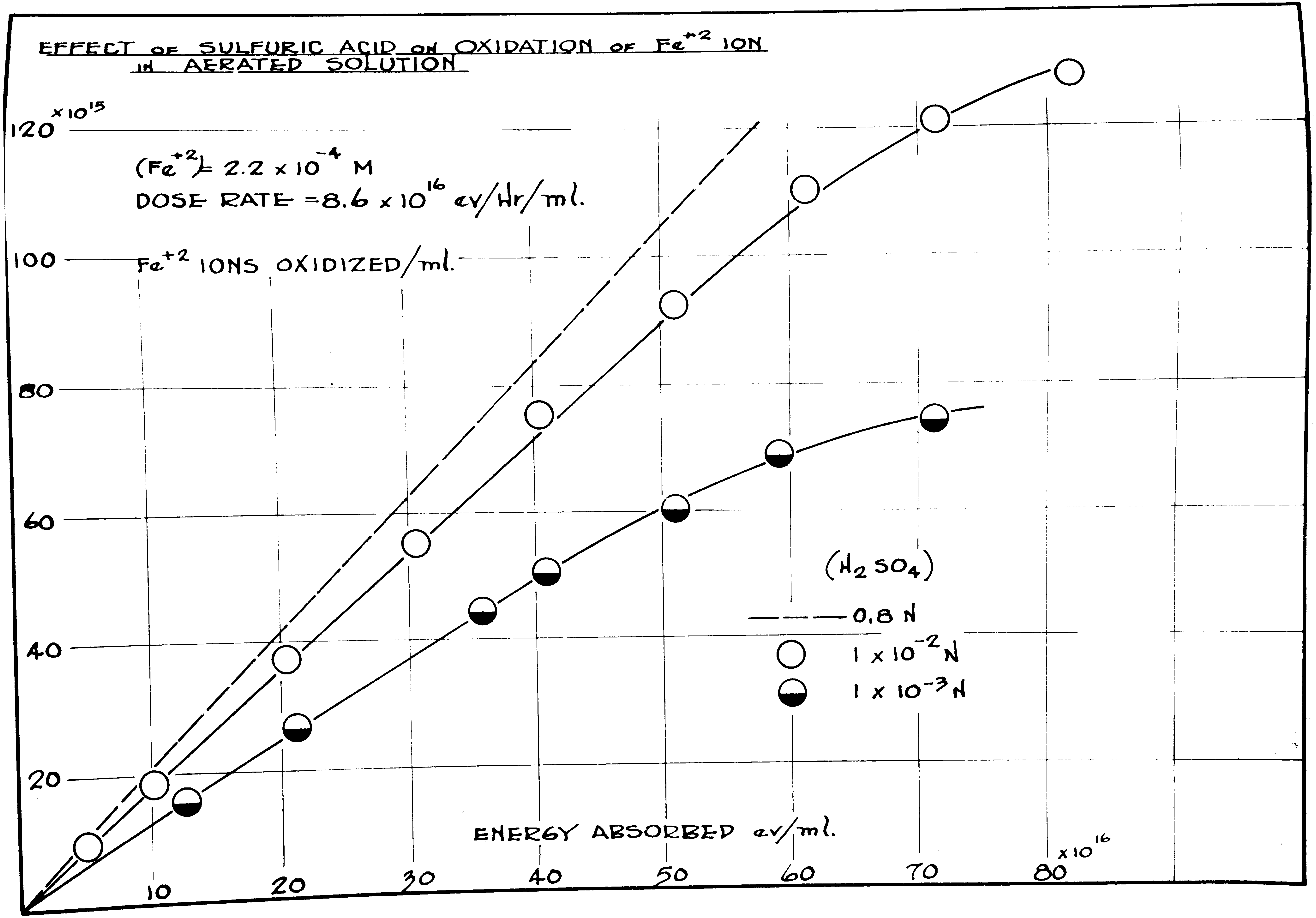

EFFECT OF SULFURIC ACID ON OXIDATION OF Fe^{+2} ION IN AERATED SOLUTION
$(Fe^{+2}) = 2.2 \times 10^{-4}$ M
DOSE RATE $= 8.6 \times 10^{16}$ ev/Hr/ml.
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
120
100
80
60
40
20
10
20
30
40
50
60
70
80
$\times 10^{16}$
ENERGY ABSORBED ev/ml.
(H_2SO_4)
0.8 N
○ 1×10^{-2} N
◒ 1×10^{-3} N

FIGURE XII

TABLE XII

Effect of Sulfuric Acid Concentration on the Oxidation of Fe^{+2} Ion in Aerated Solution

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

Dose Rate = 8.6×10^{16} ev/Hr/ml

$(H_2SO_4) = 1 \times 10^{-2}$ N		$(H_2SO_4) = 1 \times 10^{-3}$ N	
Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
4.3×10^{16}	7.6×10^{15}	4.3×10^{16}	6.9×10^{15}
8.6	15.2	8.6	11.0
12.9	22.8	12.9	16.6
17.2	29.0	17.2	22.1
21.5	37.4	25.8	31.2
25.8	43.6	34.5	36.0
34.5	47.7	42.8	39.4
		51.5	40.7

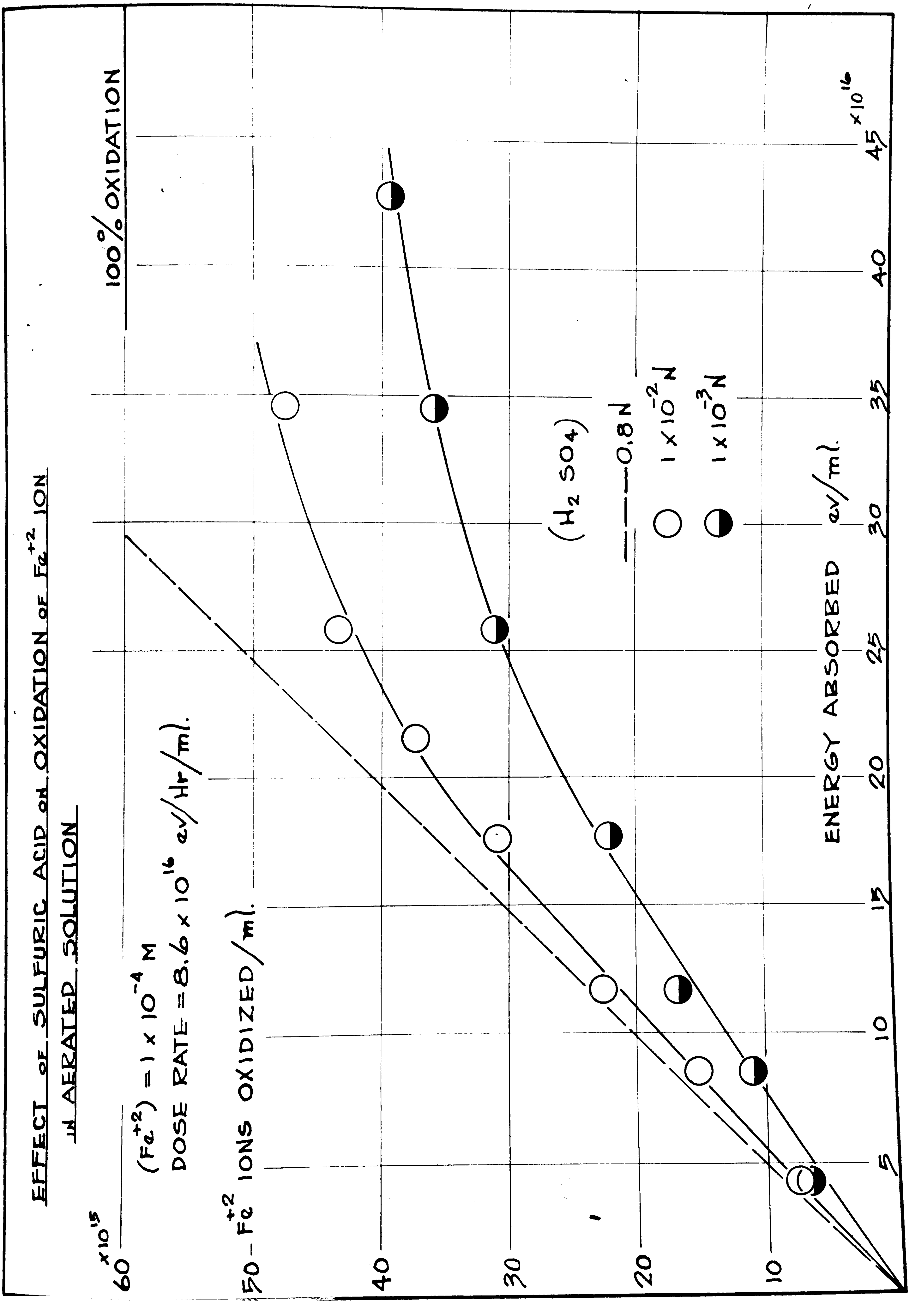

EFFECT OF SULFURIC ACID ON OXIDATION OF Fe^{+2} ION IN AERATED SOLUTION
$(Fe^{+2}) = 1 \times 10^{-4}$ M
DOSE RATE = 8.6×10^{16} ev/Hr/ml.
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
60
50
40
30
20
10
100% OXIDATION
(H_2SO_4)
— — 0.8N
○ 1×10^{-2}N
◐ 1×10^{-3}N
ENERGY ABSORBED ev/ml.
5
10
15
20
25
30
35
40
45 $\times 10^{16}$

FIGURE XIII

TABLE XIII

Effect of Adding Na_2SO_4 on the Oxidation of Fe^{+2} Ion in Aerated Solution

$(Fe^{+2}) = 1 \times 10^{-4}$ M

$(H_2SO_4) = 1 \times 10^{-3}$ N

$(Na_2SO_4) = 1.0$ M

Dose Rate = 1.0×10^{17} ev/Hr/ml

Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
5.0×10^{16}	6.3×10^{15}
10.0	13.0
15.0	19.0
20.0	25.5

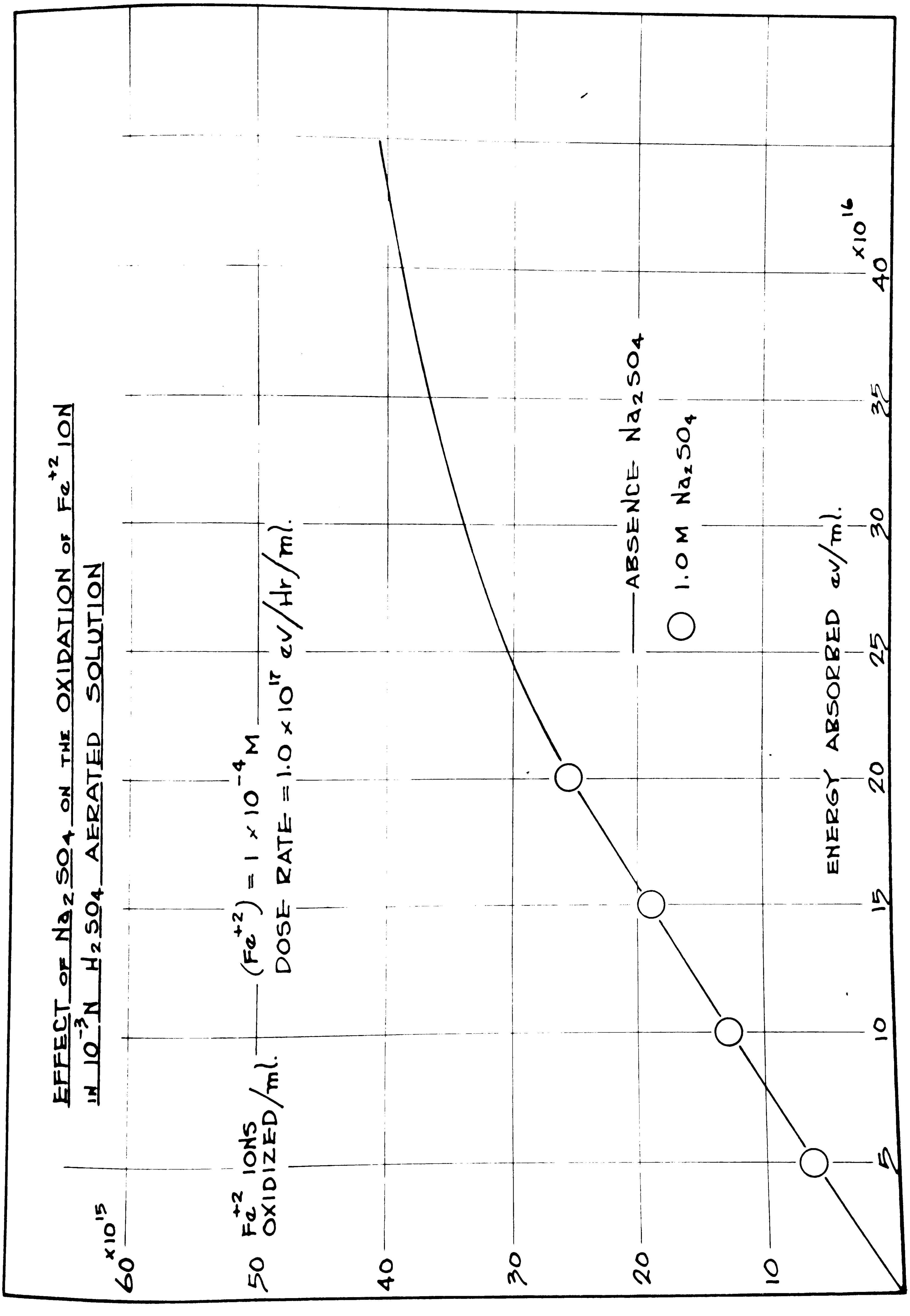

EFFECT OF Na_2SO_4 ON THE OXIDATION OF Fe^{+2} ION
IN 10^{-3}N H_2SO_4 AERATED SOLUTION
$(Fe^{+2}) = 1 \times 10^{-4}$ M
DOSE RATE = 1.0×10^{17} eV/Hr/ml.
ABSENCE Na_2SO_4
1.0 M Na_2SO_4
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
60
50
40
30
20
10
ENERGY ABSORBED eV/ml.
$\times 10^{16}$
5
10
15
20
25
30
35
40

FIGURE XIV

TABLE XIV

Initial Oxidation Yield as a Function of the Sulfuric Acid Concentration in Aerated Solution

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

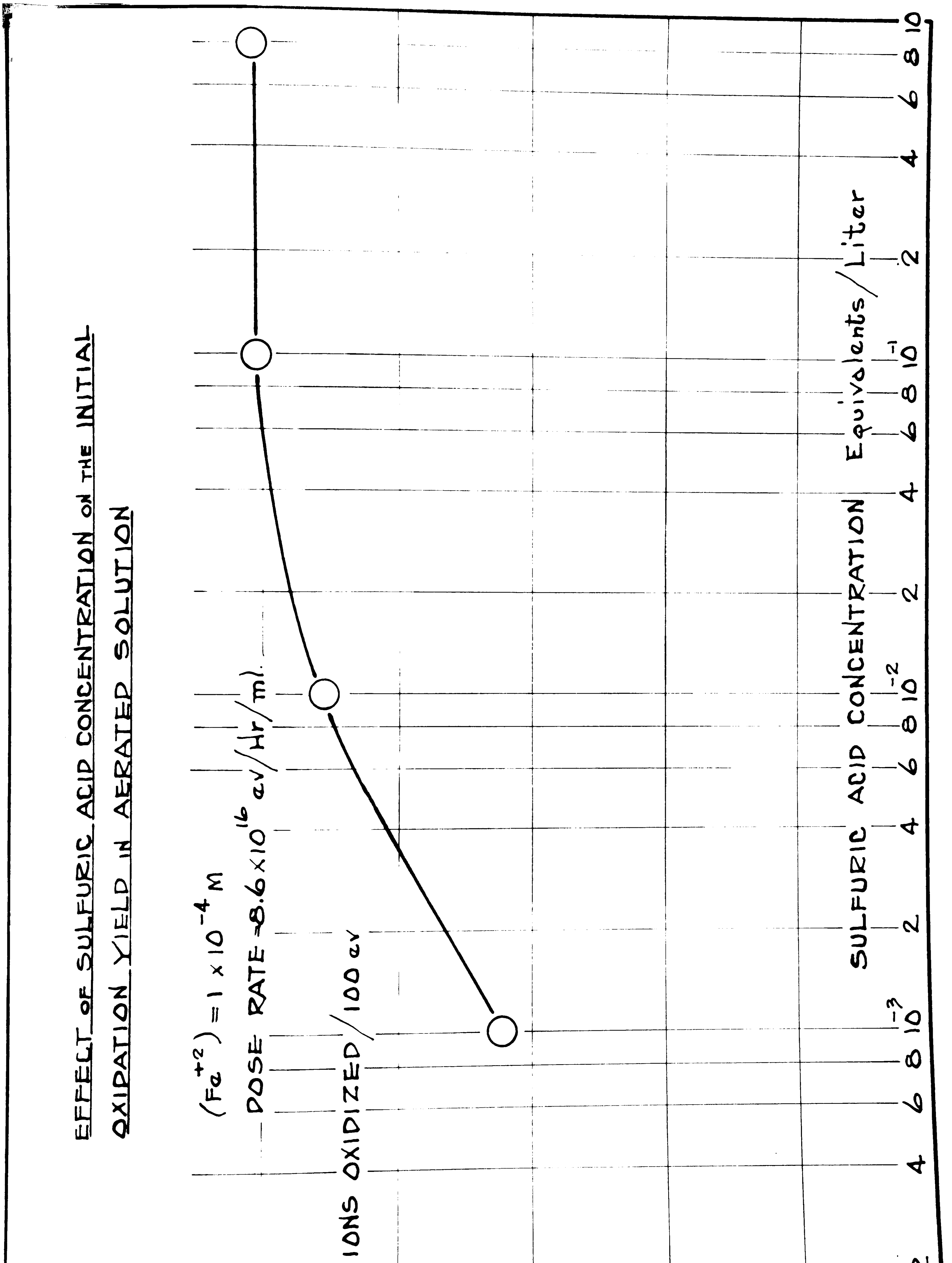
Dose Rate = 8.6×10^{16} ev/Hr/ml

(H_2SO_4) normal	Initial Oxidation Yield Fe^{+2} ions oxidized/100 ev
8×10^{-1}	20.3
1×10^{-1}	20.2
1×10^{-2}	18.2
1×10^{-3}	12.9

$(Fe^{+2}) = 2.2 \times 10^{-4}$ M

Dose Rate = 1.0×10^{17} ev/Hr/ml

(H_2SO_4) Normal	Initial Oxidation Yield Fe^{+2} ions oxidized/100 ev
8×10^{-1}	20.2
1×10^{-1}	20.3
1×10^{-2}	18.3
1×10^{-3}	12.5



EFFECT OF SULFURIC ACID CONCENTRATION ON THE INITIAL OXIDATION YIELD IN AERATED SOLUTION

FIGURE XV

Effect of Acid on the Yield-Fe^{+2} Ion Concentration Relationship

Since it was found that decrease in the acid concentration, for a given Fe^{+2} ion concentration, decreased the initial oxidation yield, it appeared important to determine what effect variation of the acid concentration had on the relation between the initial Fe^{+2} ion concentration and the initial oxidation yield. Accordingly, experiments were made to determine the initial oxidation yield as a function of the initial Fe^{+2} ion concentration in the presence of 0.01 N and 0.001 N H_2SO_4. As with 0.8 N H_2SO_4, a complete oxidation-energy absorbed curve was determined for each initial Fe^{+2} ion concentration. The initial oxidation yields were obtained from the initial slopes of these curves and are given in Table XV and Fig. XVI as a function of the initial Fe^{+2} ion concentration. In this figure the previous results for 0.8 N H_2SO_4 are included for comparison. The most striking feature of these results is the identical shape of the curves shown in Fig. XVI which show that even though the initial oxidation yield decreases with decrease in the acid concentration, yet it is independent of the initial Fe^{+2} ion concentration from 10^{-3} M to 10^{-4} M. It is also seen that for each acid concentration studied, the initial oxidation yield decreases below Fe^{+2} ion concentrations of 10^{-4} M.

TABLE XV

Effect of Acid on the Initial Oxidation Yield as a Function of the Initial Fe^{+2} Ion Concentration, in Aerated Solution

Dose Rate = 8.6 x 10^{16} ev/Hr/ml

$(H_2SO_4) = 1 \times 10^{-2}$ N

Initial (Fe^{+2}) moles/liter	Initial Oxidation Yield Fe^{+2} oxidized/100 ev
1.0 x 10^{-3}	18.3
2.4 x 10^{-4}	18.2
1.0 x 10^{-4}	18.2
5.1 x 10^{-5}	17.3
2.4 x 10^{-5}	13.9
1.0 x 10^{-5}	7.9

$(H_2SO_4) = 1 \times 10^{-3}$ N

Initial (Fe^{+2}) moles/liter	Initial Oxidation Yield Fe^{+2} oxidized/100 ev
1.0 x 10^{-3}	13.1
2.5 x 10^{-4}	13.2
1.0 x 10^{-4}	13.0
7.3 x 10^{-5}	12.4
5.0 x 10^{-5}	11.7
2.5 x 10^{-5}	9.9
1.0 x 10^{-5}	5.0

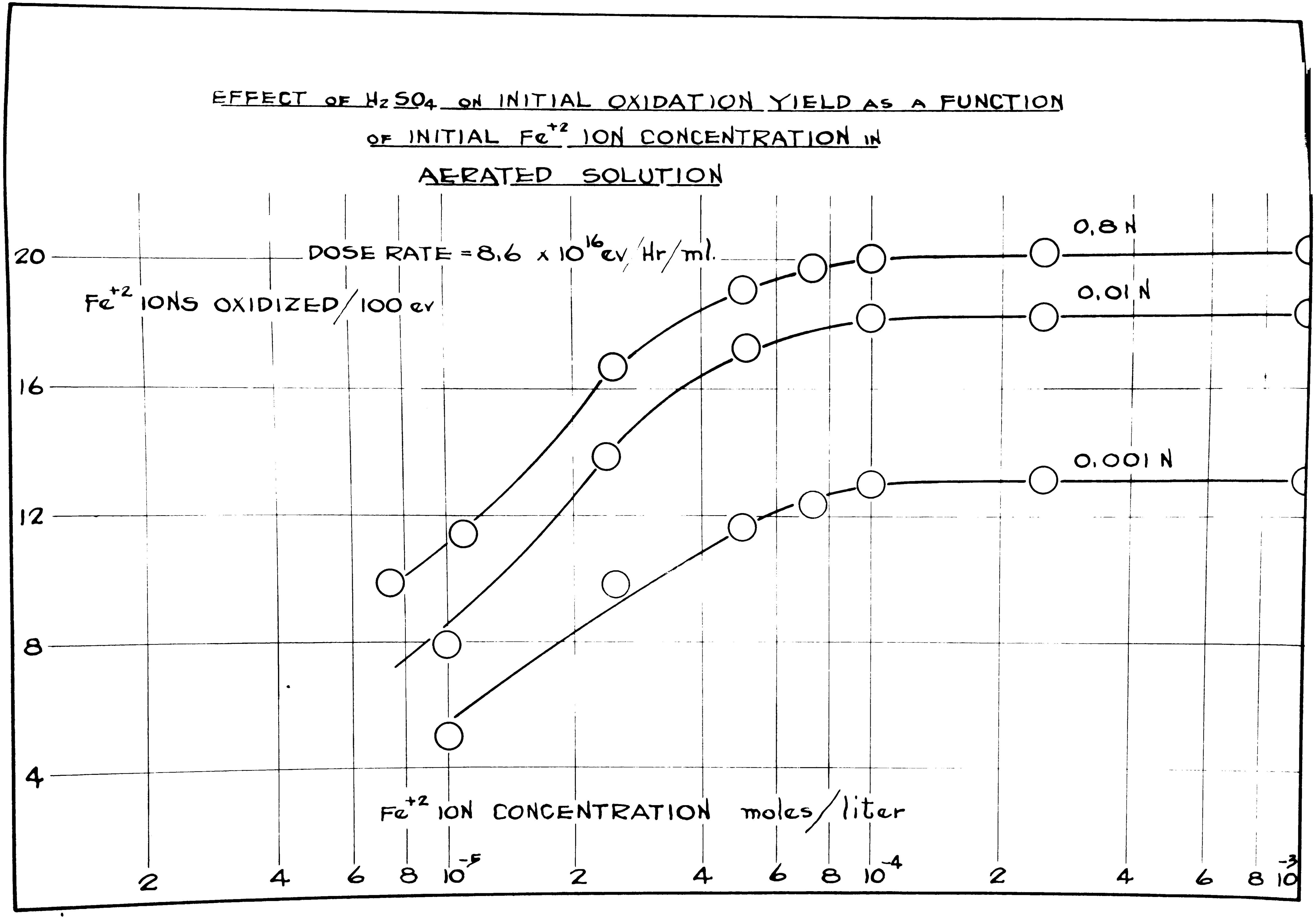

EFFECT OF H_2SO_4 ON INITIAL OXIDATION YIELD AS A FUNCTION
OF INITIAL Fe^{+2} ION CONCENTRATION IN
AERATED SOLUTION
DOSE RATE = 8.6 x 10^{16} ev/Hr/ml.
Fe^{+2} IONS OXIDIZED/100 ev
0.8 N
0.01 N
0.001 N
20
16
12
8
4
Fe^{+2} ION CONCENTRATION moles/liter
2
4
6
8
10^{-5}
2
4
6
8
10^{-4}
2
4
6
8
10^{-3}

FIGURE XVI

Studies in the Fall-Off Region in 0.8 N Sulfuric Acid

(a) Effect of heating irradiated samples prior to analysis.

Further investigation of the oxidation of Fe^{+2} ion at concentrations below 1×10^{-4} M, i.e., in the region of decreased yield, revealed that heating the irradiated solutions prior to analysis produced additional oxidation of Fe^{+2} ions. The results of these experiments are recorded in Table XVI and Fig. XVII. For this figure (also Figs. XVIII and XIX), the data for the upper curve was obtained by heating the solution at 70°C for two minutes prior to analysis; that for the middle curve was obtained by analyzing the solution immediately on removal from the γ-radiation (normal analysis); the lower curve is a plot of the difference between the heated and normal analysis. Control experiments with unirradiated Fe^{+2} ion solutions showed that no oxidation of Fe^{+2} ion occurred when these solutions were heated to 70°C for two minutes. These results show that the initial oxidation yield is increased to the value corresponding to the yield for the concentration independence region. The lower curves in these figures show that the accumulation of oxidant is initially a linear function of the energy absorbed and that the oxidant attains an equilibrium concentration. It is seen that when the equilibrium concentration is attained, the oxidation of Fe^{+2} ion is apparently first order.

TABLE XVI

Effect of Heating Irradiated Solutions on the Oxidation of Fe^{+2} Ion in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 4.6 \times 10^{-5}$ M

Dose Rate = 9.5×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
2.37×10^{16}	3.31×10^{15}
	4.64*
4.74	7.90
	9.40*
7.12	12.0
	14.6*
9.45	15.9
	18.7*
11.9	19.5
	22.5*
14.2	22.2
	25.4*
16.6	25.0
	27.8*

* These samples were heated to 70°C prior to analysis.

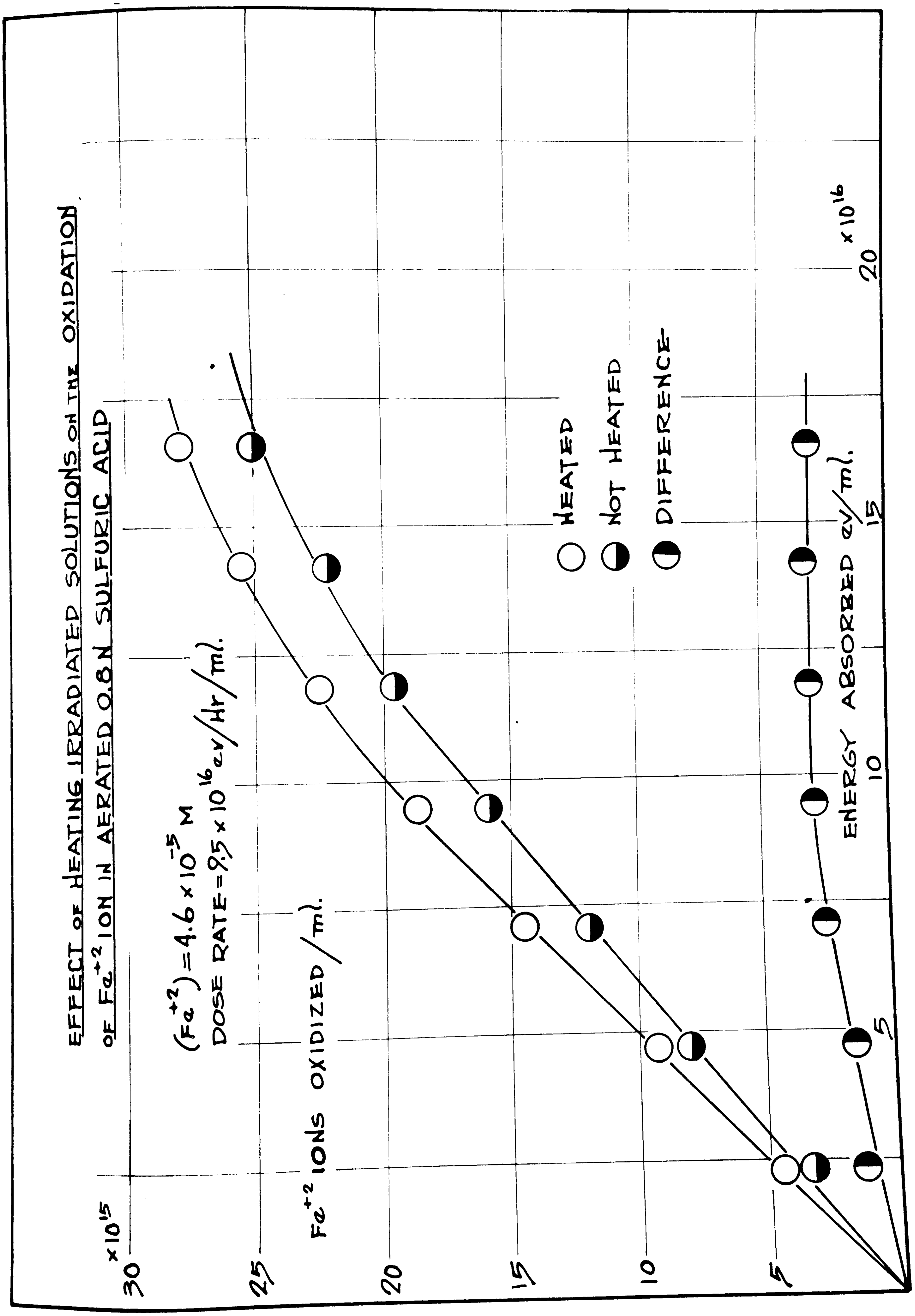

EFFECT OF HEATING IRRADIATED SOLUTIONS ON THE OXIDATION
OF Fe+2 ION IN AERATED 0.8N SULFURIC ACID
(Fe+2)=4.6×10-5 M
DOSE RATE=9.5×1016 ev/Hr/ml.
Fe+2 IONS OXIDIZED/ml.
×1015
30
25
20
15
10
5
ENERGY ABSORBED ev/ml.
×1016
5
10
15
20
HEATED
NOT HEATED
DIFFERENCE

FIGURE XVII

In the absence of any confirmatory evidence the above results suggest that the oxidant which accumulates in the solution is probably hydrogen peroxide. In view of these results, it appeared that at a lower dose rate the effect of heating should be decreased, i.e., the time to absorb a given energy would be increased, which would then permit the reaction between Fe^{+2} ion and H_2O_2 to be more complete. The results of this experiment are given in Table XVII and Fig. XVIII. A comparison of this data with that given in Table XVI and Fig. XVII shows that decreasing the dose rate by a factor of 2.6 decreased the effect of heating. As in the previous experiment, the effect of heating the irradiated solution is to increase the initial oxidation yield to that for the concentration independence region. In addition, a comparison of the middle curves in Figs. XVII and XVIII indicates that the initial oxidation yield is apparently inversely proportional to the dose rate. At a dose rate of 9.5×10^{16} ev/Hr/ml the initial yield for the accumulation of excess oxidant is 1.7 H_2O_2 molecules/100 ev and attains a steady state concentration of 1.5×10^{15} molecules/ml, whereas at a dose rate of 3.6×10^{16} ev/Hr/ml the initial yield for the accumulation of excess oxidant is 0.9 H_2O_2 molecules/100 ev and attains a steady state concentration of 0.7×10^{15} molecules/ml.

The effect of Fe^{+2} ion concentration on the accumulation of excess oxidant in the fall-off region was investigated at a constant dose rate of 3.6×10^{16} ev/Hr/ml. This data was obtained from Tables XVII and XVIII and Figs. XVIII and XIX. It was found that decreasing the Fe^{+2} ion concentration from 4.6×10^{-5} M to 2.6×10^{-5} M had no

TABLE XVII

Effect of Heating Irradiated Solutions on the Oxidation of Fe^{+2} Ion in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 4.6 \times 10^{-5}$ M

Dose Rate = 3.6×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml
1.82×10^{16}	3.61×10^{15}
	4.26*
3.63	7.30
	7.95*
5.45	10.9
	11.9*
7.28	14.1
	15.2*
9.04	17.8
	19.2*
10.9	20.2
	21.5*
12.7	23.4
	24.8*
14.5	25.6
	27.1*

* These samples were heated to 70°C prior to analysis.

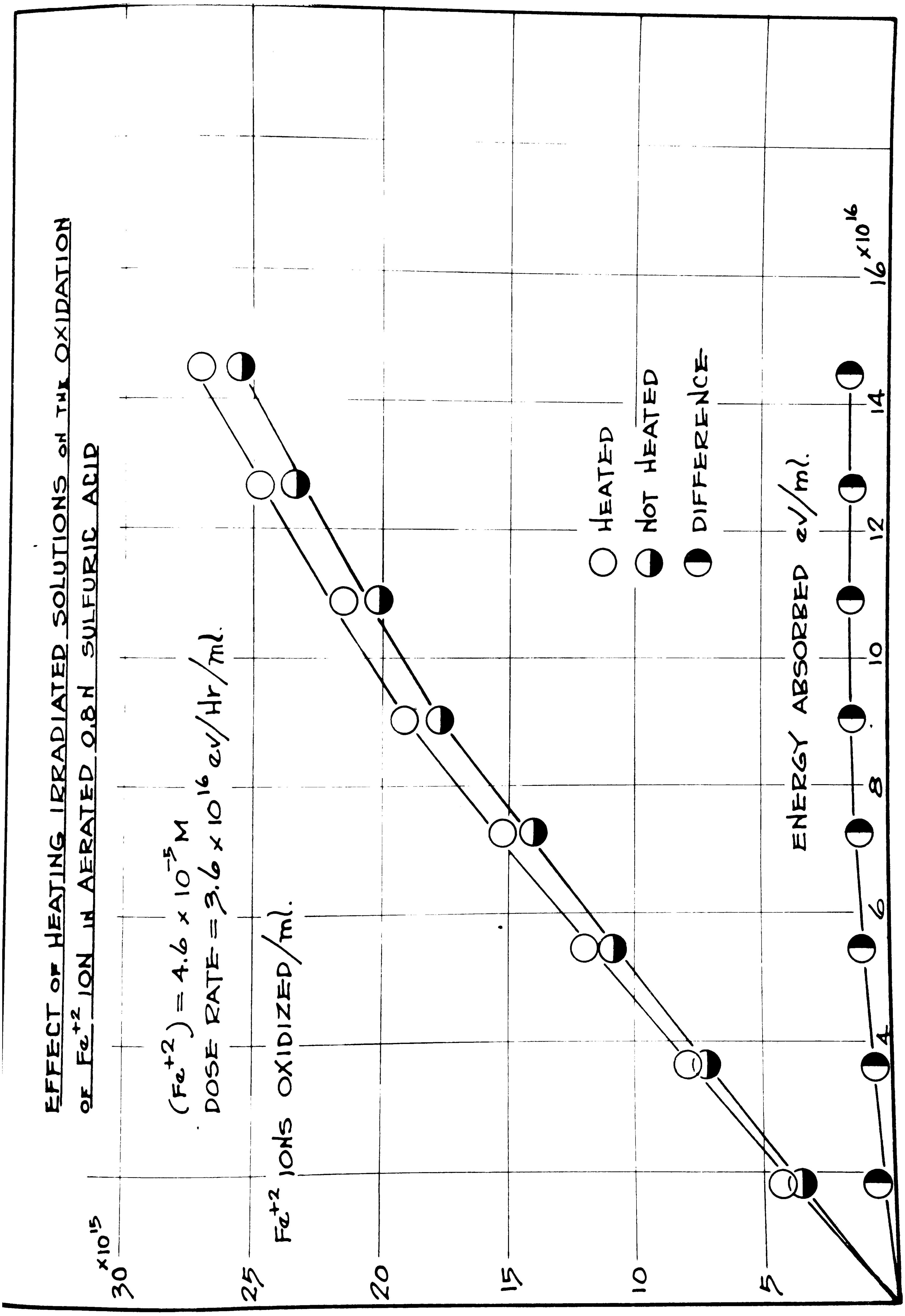


FIGURE XVIII

TABLE XVIII

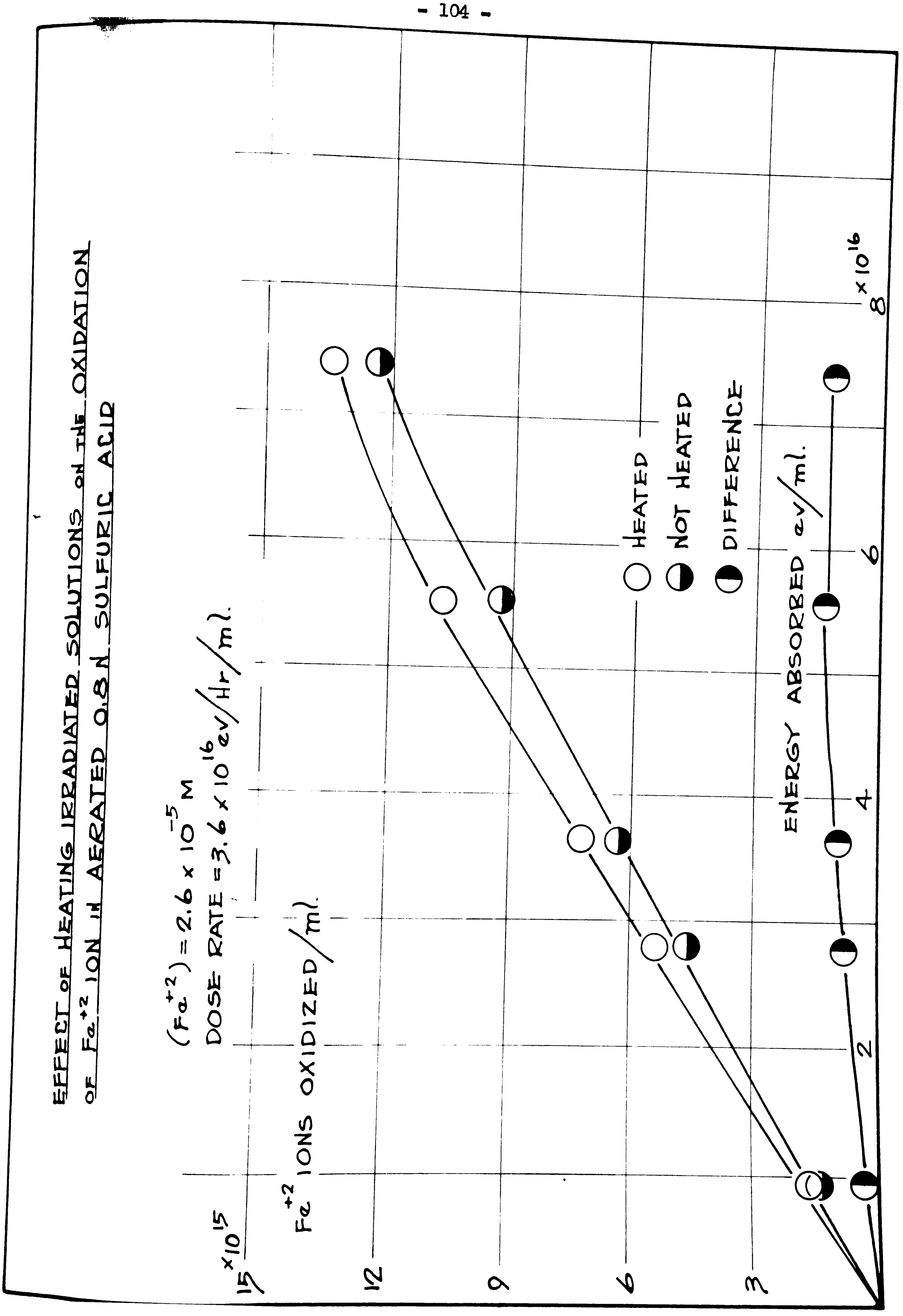
Effect of Heating Irradiated Solutions on the Oxidation of Fe^{+2} Ion in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 2.6 \times 10^{-5}$ M

Dose Rate = 3.6×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	$\triangle (Fe^{+2})$ ions/ml
0.93×10^{16}	1.32×10^{15}
	1.62*
2.78	4.64
	5.41*
3.69	6.34
	7.24*
5.55	9.35
	10.7*
7.40	12.4
	13.5*

* These samples were heated to 70°C prior to analysis.



EFFECT OF HEATING IRRADIATED SOLUTIONS ON THE OXIDATION OF Fe^{+2} ION IN AERATED 0.8 N SULFURIC ACID

FIGURE XIX

effect on the accumulation of oxidant. That is, the initial yield and steady state concentration for the accumulation of excess oxidant were identical, within the experimental error, for both Fe^{+2} ion concentrations. Hence, the accumulation of excess oxidant in the fall-off region appears to be independent of the Fe^{+2} ion concentration.

(b) Effect of dose rate on the oxidation of Fe^{+2} ion.

The data for the effect of dose rate on the oxidation of Fe^{+2} ion, for solutions that were not heated prior to analysis, are recorded in Table XIX and shown graphically in Fig. XX. The curves in this figure indicate that the initial oxidation yield varies inversely as the dose rate, that is, decrease in dose rate increases the initial oxidation yield.

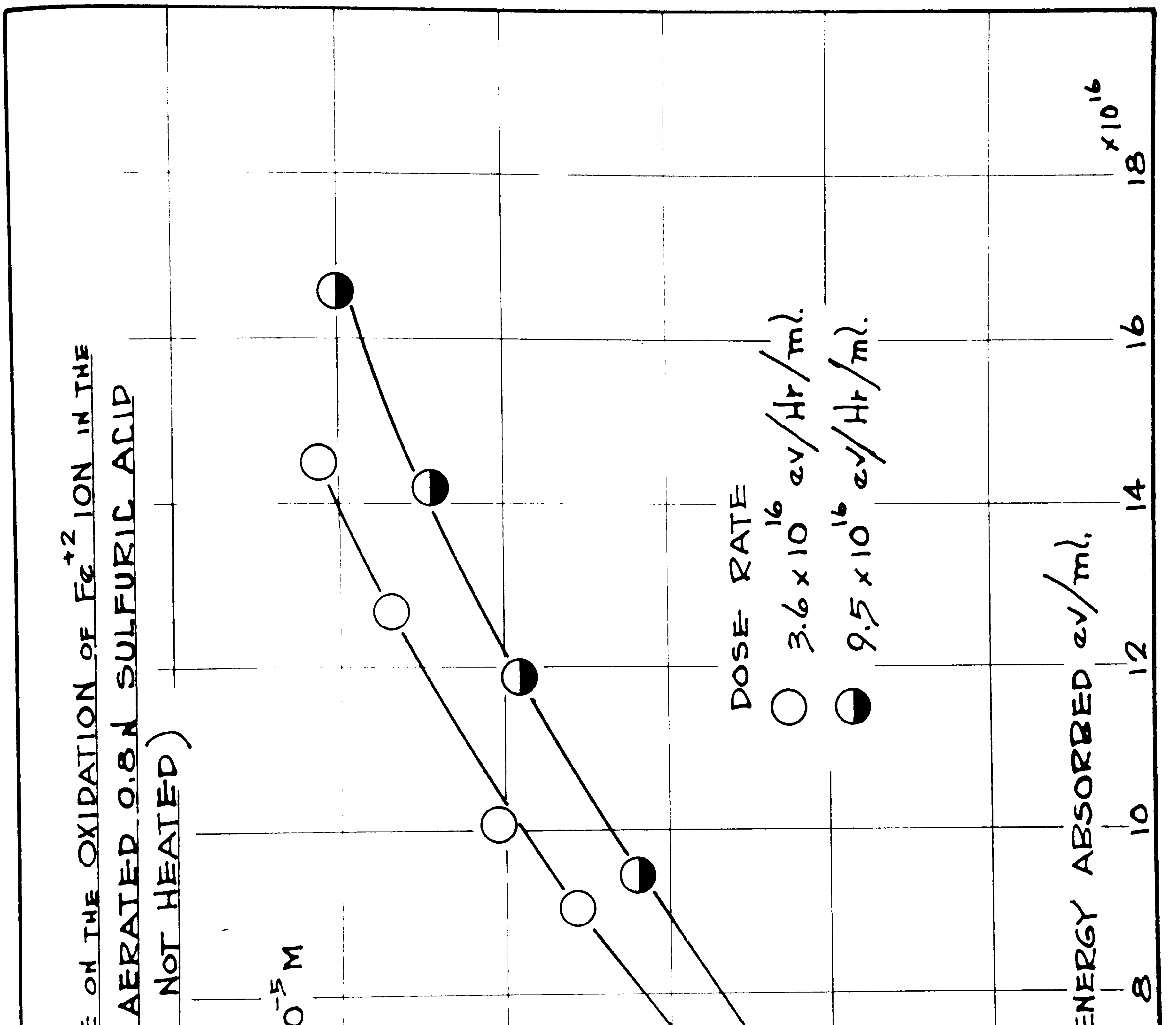
A comparison of the initial oxidation yields for the heated samples in Figs. XVIII and XIX indicates approximately a 6% discrepancy in the initial oxidation yields. Since this is probably within the experimental error, it may be concluded that for the heated samples there is no effect of dose rate on the initial oxidation yield. This result should be compared with the observation that the initial oxidation yield for solutions of concentration greater than 10^{-4} M is independent of dose rate.

TABLE XIX

Effect of Dose Rate on the Oxidation of Fe^{+2} Ion in Aerated Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 4.6 \times 10^{-5}$ M

Dose Rate = 9.5×10^{16} ev/Hr/ml		Dose Rate = 3.6×10^{16} ev/Hr/ml	
Energy Absorbed ev/ml	$\triangle(Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\triangle(Fe^{+2})$ ions/ml
2.37×10^{16}	3.3×10^{15}	1.82×10^{16}	3.6×10^{15}
4.74	7.9	3.63	7.3
7.12	12.0	5.45	10.9
9.45	15.9	7.28	14.1
11.9	19.5	9.04	17.8
14.2	22.2	10.9	20.2
16.6	25.0	12.7	23.4
		14.5	25.6



EFFECT OF DOSE RATE ON THE OXIDATION OF Fe^{+2} ION IN THE FALL OFF REGION IN AERATED 0.8 N SULFURIC ACID
(SAMPLES NOT HEATED)
$(Fe^{+2}) = 4.6 \times 10^{-5}$ M
Fe^{+2} IONS OXIDIZED/ml.
$\times 10^{15}$
30
25
20
15
10
5
ENERGY ABSORBED ev/ml.
2
4
6
8
10
12
14
16
18
$\times 10^{16}$
DOSE RATE
○ 3.6×10^{16} ev/Hr/ml.
◐ 9.5×10^{16} ev/Hr/ml.

FIGURE XX

(B) AIRFREE SOLUTION

Airfree solutions are those with which extreme precautions were taken to remove completely all the dissolved air. Preliminary experiments indicated that merely evacuating the solutions for a short period of time did not give reproducible results. However, these experiments did show that the removal of a large fraction of the dissolved air considerably reduced the oxidation yield. Hence, it appeared most important to study the oxidation of Fe^{+2} ion in the complete absence of dissolved air.

The complete removal of dissolved gases from liquids has been the subject of much experimental investigation. The methods generally employed for removal of the common gases (oxygen, carbon dioxide, nitrogen, etc.) from water are boiling, heating under reduced pressure and bubbling an inert gas through the water. However, it is not certain that these methods effectively remove the last traces of oxygen. An extremely elaborate and effective procedure was devised by Taylor (73) for removal of dissolved oxygen. His method consisted of fractional distillation under vacuum and required several days to produce a small quantity of oxygen-free water. A relatively simple method was employed by Hibben (74) for the complete removal of dissolved gases from water. In effect, his method was vacuum sublimation, i.e., the liquid to be freed from dissolved gases was vaporized and frozen in vacuo. Hibben points out the following criteria for the efficient removal of dissolved gas. (a) The temperature at the condensing surface should be considerably lower than the freezing point of the liquid, i.e., the vapor condenses directly to solid. (b) The sublimate must have a negligible vapor pressure at the condensation temperature, to prevent loss of the liquid. (c) The vapor pressure of the gas which can exist on the condenser must be greater than the partial pressure of the gas in the gas phase. Using liquid air as the coolant, Hibben states that one vacuum sublimation reduces the concentration of dissolved oxygen in water to one ten thousandth of 1%.

It was observed by Miller (49) that a solution of Fe^{+2} ion equilibrated with tank N_2, containing about 2% O_2, was oxidized by γ-radiation within a few precent of the yield for an oxygen equilibrated solution. He concluded from this experiment "that very little oxygen was necessary to saturate the solution effectively with oxygen from the radiation chemical point of view".

This observation, and the fact that preliminary experiments employing a simple evacuation procedure did not give reproducible results, suggested a more elaborate method for deaeration, which is described in the following section.

Deaeration Procedure

The preliminary experiments indicated a need for a method whereby all the dissolved air was completely and effectively removed from the solution. Only in this way could a quantitative study be made of the kinetics in airfree solutions. Since merely evacuating the solution with an ordinary mechanical vacuum pump appeared to be ineffective, this suggested the use of a high vacuum, high pumping speed system. With this in view the apparatus shown in Fig. XXI was assembled and proved to be effective in the deaeration of the solutions.

The apparatus was constructed of 25 mm. O.D. pyrex tube and assembled in such a way as to minimize right angle bends, which are detrimental to the attainment of a high pumping speed. The pumping system consisted of a high speed mercury diffusion pump, rated at 16 liters/sec. at 10^{-4} mm. Hg, backed by a mechanical vacuum pump (Welch Duoseal). In the diagram, s is a large bore (20 mm.) straight-through type high vacuum stopcock. The vacuum gauge, a, is a commercial type ion gauge (VG1A, Distillation Products) and p a commercial type Pirani gauge (Distillation Products) each with their respective control circuits. The Pirani gauge was calibrated with dry air against a rotating-type McLeod gauge. The traps, t_1 and t_2, are of the Dewar type. M is the vessel, henceforth referred to as the 'monster', which contained the solution to be deaerated. The monster was made from a 6 inch length of 45 mm. pyrex tube and had six identical irradiation tubes sealed around the upper half of the vessel.

The deaeration procedure was as follows. The monster, containing the solution to be deaerated, was sealed to the vacuum line at b. With liquid nitrogen in the traps t_1 and t_2, the system was evacuated with the mechanical pump until the pressure, as indicated on the Pirani gauge, was less than 20 microns. In an early experiment the monster, containing Fe^{+2} solution, was tested for leaks with a Tesla coil, and it was found that this completely oxidized the Fe^{+2} ion. In view of this, the system was always tested for leaks prior to filling the monster with Fe^{+2} solution. When the pressure was less than 20 microns, the diffusion pump was turned on. To speed

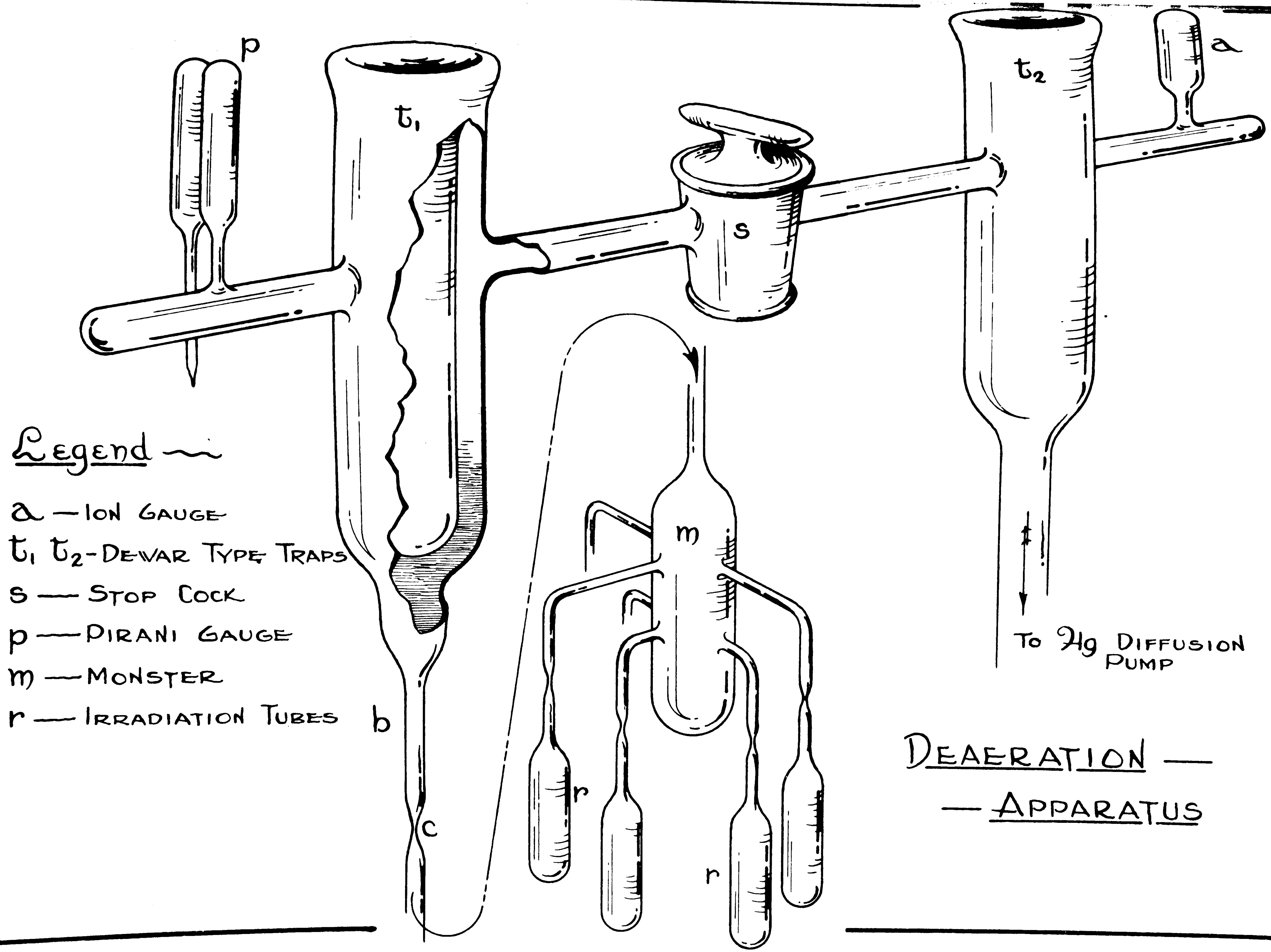

p
t₁
s
t₂
a
m
b
c
r
r
To Hg Diffusion Pump
Legend ~
a — Ion Gauge
t₁ t₂ - Dewar Type Traps
s — Stop Cock
p — Pirani Gauge
m — Monster
r — Irradiation Tubes
Deaeration — — Apparatus

FIGURE XXI

up the process of deaeration it was advantageous to heat the solution periodically and gently. When trap t_1 became heavily coated with ice, stopcock s was closed, the trap warmed up and the water then dripped back into the monster. The cycle of heating, condensing and warming trap t_1 was repeated several times throughout a period of 3 hours. When the pressure as indicated on the ion gauge was of the order of 10^{-5} mm. Hg, the monster was sealed off from the vacuum line at c. The solution in the monster was then shaken for several minutes, allowing it to flow in and out of the irradiation tubes, to ensure uniform concentration in the solution. The irradiation tubes were then filled successively with the solution to a calibrated volume (4 ml.) and sealed off. These tubes were then ready for irradiation as described in Part A. Subsequent experiments have shown that sealing off the tubes while still wet with the Fe^{+2} solution had no effect on the oxidation reaction. This was checked by deaerating a solution in the usual way, filling three of the tubes and allowing them to drain for 18 hours before sealing off, and then comparing the oxidation yield for these solutions with that for the three remaining tubes which were filled and sealed off immediately. The monster was opened and the concentration of Fe^{+2} ion determined. The above method of deaeration was found to have no effect on the concentration of Fe^{+2} ion, that is to say, the Fe^{+2} ion concentration before and after the deaeration procedure was the same. The remaining solution was saturated with air and irradiated. In this way, the ratio of the oxidation yields in airfree and aerated solution could be accurately compared under various experimental conditions.

Effect of Fe^{+2} Ion Concentration on Yield in 0.8 N H_2SO_4

Previous studies on the oxidation of Fe^{+2} ion in presumably airfree solution had indicated that the oxidation yield was a factor of 2 to 3 (average 2.5) less than the yield in aerated solution. However, the deaeration procedure usually consisted of simply boiling the solution, or evacuating with a water aspirator or mechanical vacuum pump. Thus, it appears very unlikely that the method of deaeration used in these studies could remove the last traces of dissolved air. It is questionable, therefore, whether the results of previous work on the oxidation of Fe^{+2} ion in airfree solution can be considered valid.

For this investigation the oxidation of Fe^{+2} ion was studied as a function of the initial Fe^{+2} ion concentration from 10^{-3} M to 10^{-5} M in 0.8 N H_2SO_4. These results are recorded in Tables XX, XXI and XXII and Figs. XXII, XXIII, XXIV, XXV, XXVI and XXVII. These results show that over the complete range of Fe^{+2} ion concentrations studied, the number of Fe^{+2} ions oxidized is initially a linear function of the energy absorbed by the solution. Above approximately 50% oxidation, the yield gradually decreased and appeared to approach an equilibrium concentration near to complete oxidation. In no case, however, was complete oxidation observed. In contrast to the results for aerated solutions, it is seen that the oxidation is not a linear function of the energy absorbed to 100% oxidation. In this connection it is important to note that the ratio of the liquid volume to the gas volume, in the irradiation tubes, was approximately unity. From Henry's law, the mole fraction of any gaseous product dissolved in the solution would be proportional to its partial pressure.

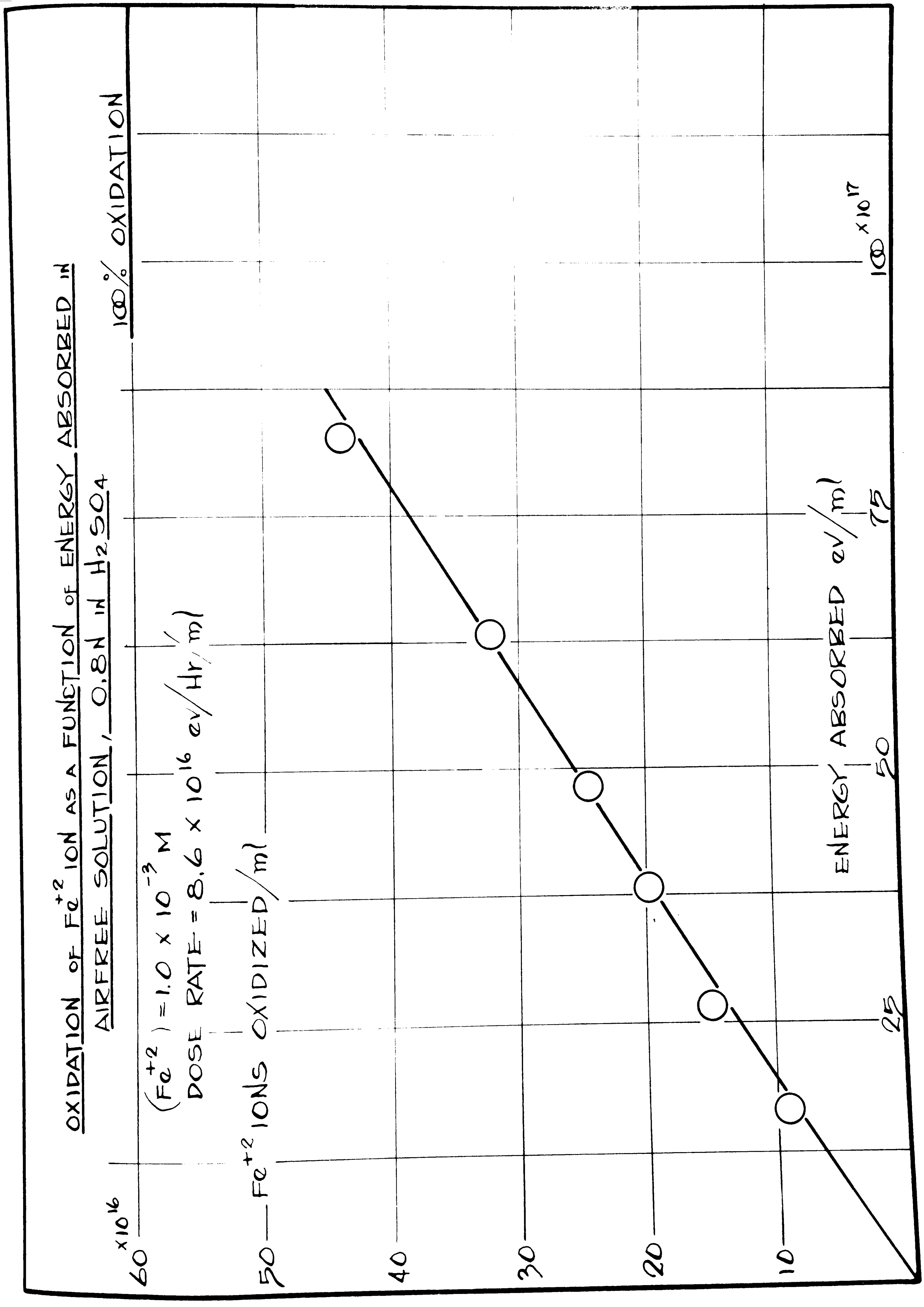
The initial oxidation yields were obtained from the initial slopes of the above curves. These results are given in Table XXIII and Fig. XXVIII (semi-log plot), from which it is seen that the initial oxidation yield is 5.1 ± 0.2 Fe^{+2} ions oxidized/100 ev, independent of the initial Fe^{+2} ion concentration from 10^{-3} M to 10^{-4} M. Below the latter concentration the initial oxidation yield decreased rapidly and at approximately 4.0×10^{-5} M Fe^{+2} ion concentration once again became independent of the initial Fe^{+2} ion concentration. Nevertheless, it was found that throughout this region, i.e., 10^{-4} M to 10^{-5} M Fe^{+2} ion concentration, the oxidation was a linear function of the energy absorbed to approximately 50% oxidation. This indicated that even though the initial oxidation yield was a function of the initial Fe^{+2} ion concentration, it was independent of the instantaneous Fe^{+2} ion concentration. These results are seen to be strikingly similar to those obtained in aerated solution below an initial Fe^{+2} ion concentration of 10^{-4} M.

TABLE XX

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Airfree Solution, 0.8 N in Sulfuric Acid

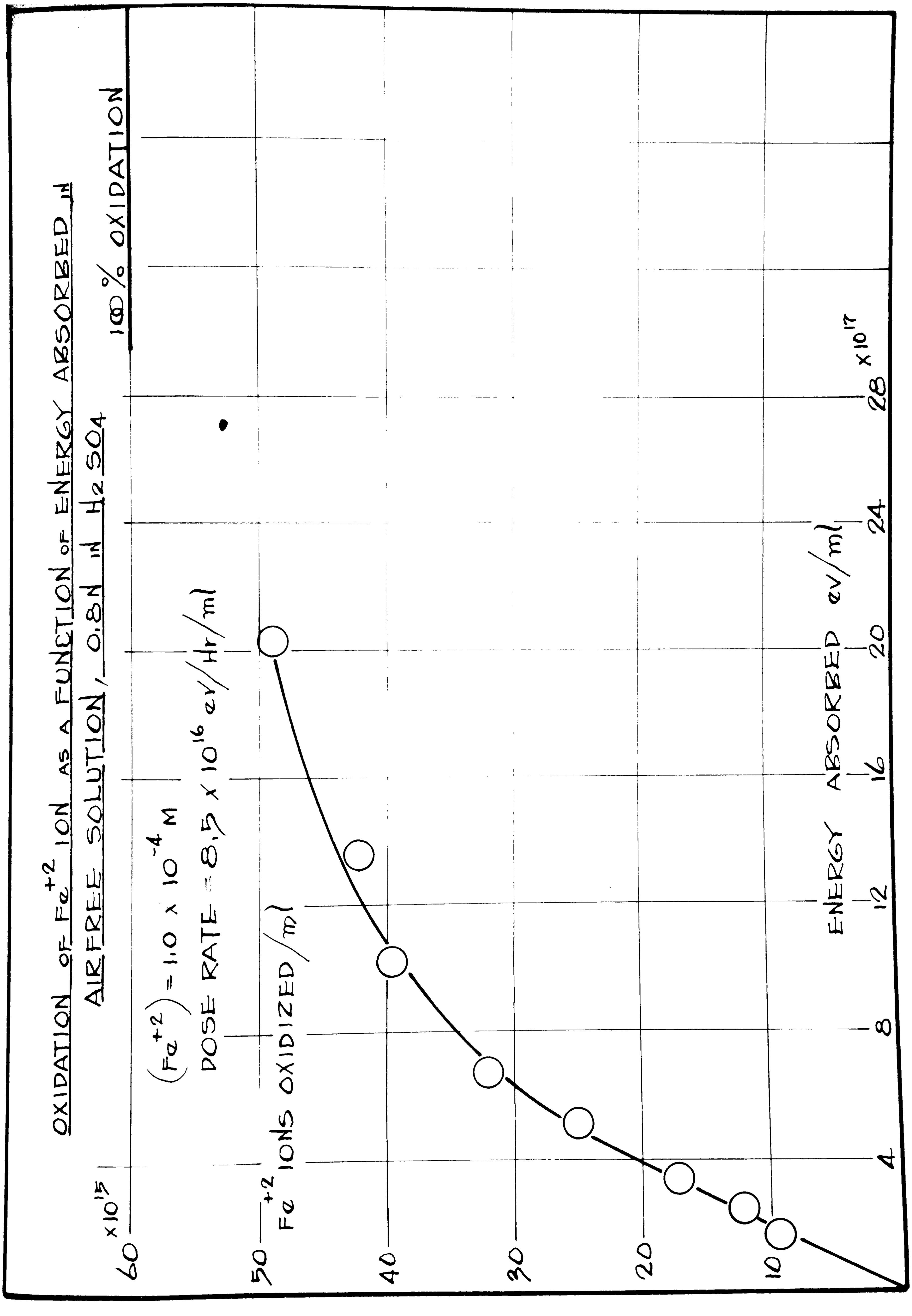
Dose Rate = 8.6×10^{16} ev/Hr/ml

$(Fe^{+2}) = 1.0 \times 10^{-3}$ M		$(Fe^{+2}) = 1.0 \times 10^{-4}$ M	
Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml
16.6×10^{17}	9.3×10^{16}	1.7×10^{17}	9.5×10^{15}
26.4	15.0	2.5	12.1
38.0	19.8	3.4	17.3
48.0	24.5	5.1	25.0
63.0	32.1	6.7	30.2
82.5	44.0	10.2	39.7
		13.6	42.3
		20.3	49.0



OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED IN AIRFREE SOLUTION, 0.8N IN H_2SO_4

FIGURE XXII



OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED IN AIRFREE SOLUTION, 0.8N IN H_2SO_4

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

DOSE RATE = 8.5×10^{16} eV/Hr/ml

FIGURE XXIII

TABLE XXI

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Airfree Solution, 0.8 N in Sulfuric Acid

Dose Rate = 8.5×10^{16} ev/Hr/ml

$(Fe^{+2}) = 7 \times 10^{-5}$ M		$(Fe^{+2}) = 4.7 \times 10^{-5}$ M	
Energy Absorbed ev/ml	$\triangle (Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\triangle (Fe^{+2})$ ions/ml
1.7×10^{17}	6.6×10^{15}	1.7×10^{17}	4.6×10^{15}
2.5	9.9	3.4	9.3
3.4	11.9	5.1	12.6
5.1	18.0	6.8	17.2
6.3	20.2	8.5	20.6
16.1	35.7	10.2	21.2

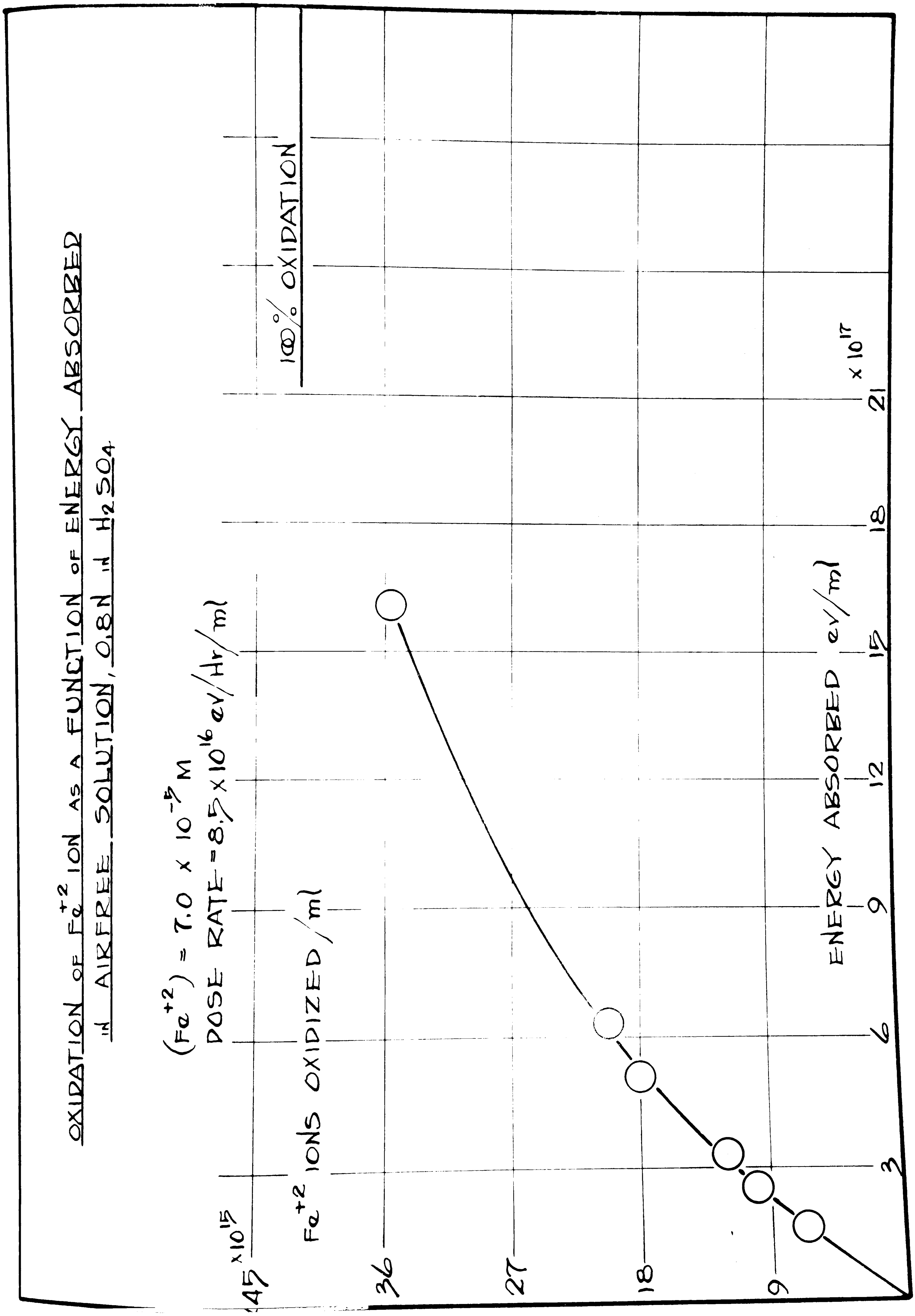

OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED
IN AIRFREE SOLUTION, 0.8N IN H_2SO_4
$(Fe^{+2}) = 7.0 \times 10^{-5}$ M
DOSE RATE = 8.5×10^{16} eV/Hr/ml
Fe^{+2} IONS OXIDIZED/ml
$\times 10^{15}$
45
36
27
18
9
100% OXIDATION
ENERGY ABSORBED eV/ml
3
6
9
12
15
18
21
$\times 10^{17}$

FIGURE XXIV

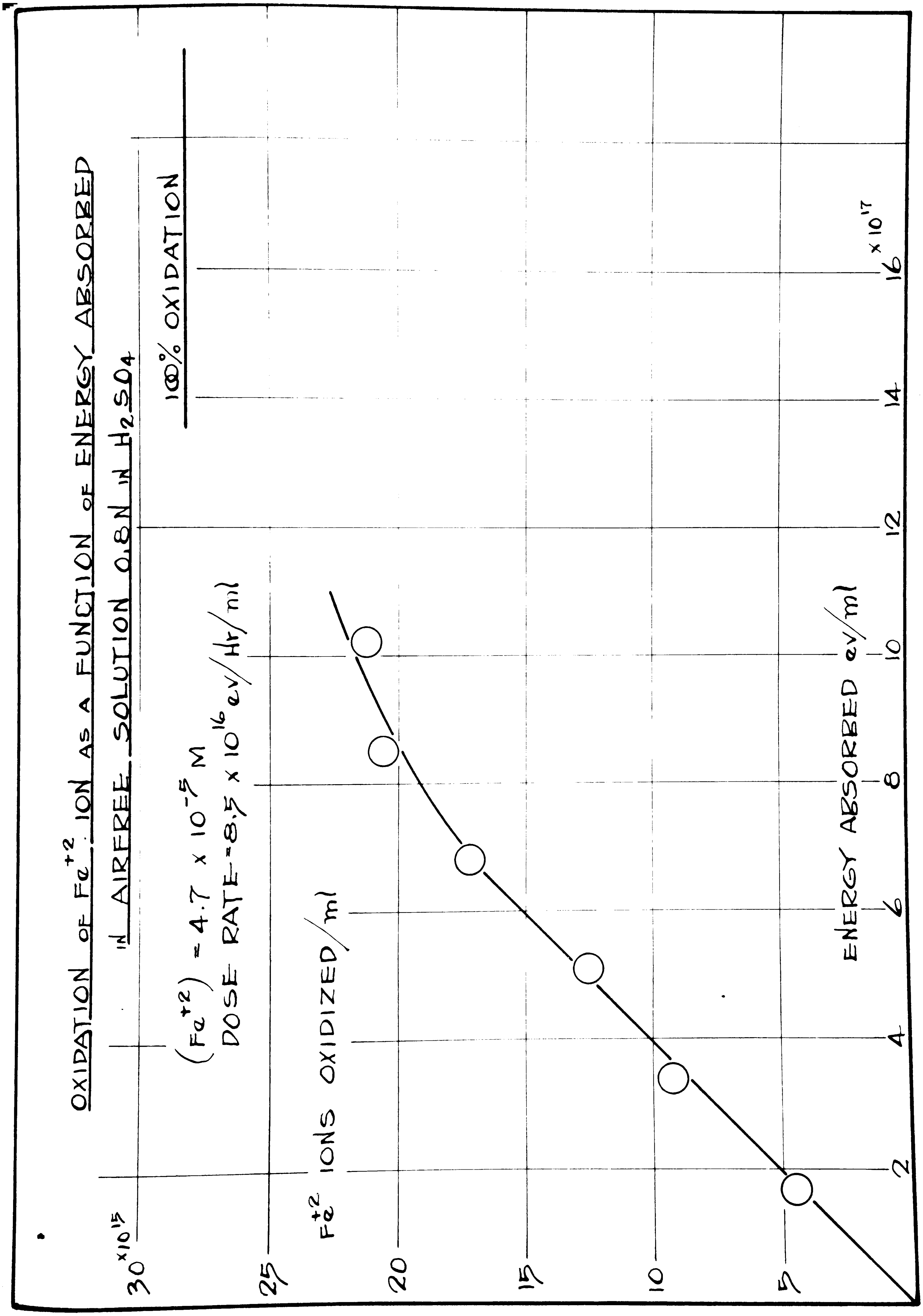

OXIDATION OF Fe+2 ION AS A FUNCTION OF ENERGY ABSORBED
IN AIRFREE SOLUTION 0.8N IN H2SO4
100% OXIDATION
(Fe+2) = 4.7 x 10-5 M
DOSE RATE = 8.5 x 10^16 ev/Hr/ml
Fe+2 IONS OXIDIZED/ml
30 x10^15
25
20
15
10
5
ENERGY ABSORBED ev/ml
2
4
6
8
10
12
14
16 x 10^17

FIGURE XXV

TABLE XXII

Oxidation of Fe^{+2} Ion as a Function of Energy Absorbed in Airfree Solution, 0.8 N in Sulfuric Acid

Dose Rate = 8.5×10^{16} ev/Hr/ml

$(Fe^{+2}) = 3.5 \times 10^{-5}$ M		$(Fe^{+2}) = 1.9 \times 10^{-5}$ M	
Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta (Fe^{+2})$ ions/ml
1.4×10^{17}	3.1×10^{15}	8.5×10^{16}	2.2×10^{15}
2.6	4.6	17.0	4.3
3.4	6.9	25.4	5.9
5.1	8.6	34.0	7.3
6.8	10.2	42.5	8.6
		53.1	8.3

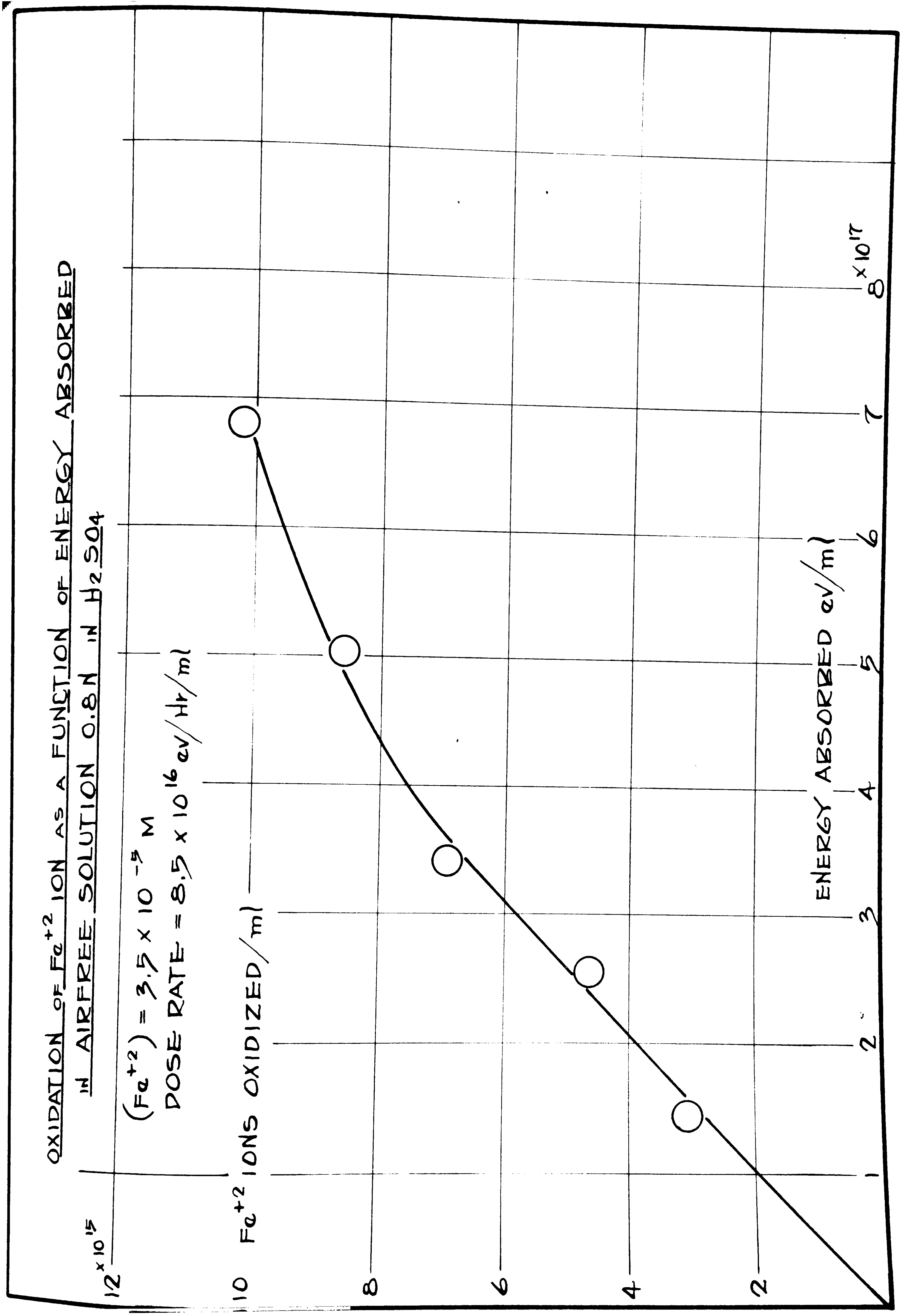

OXIDATION OF Fe^{+2} ION AS A FUNCTION OF ENERGY ABSORBED
IN AIRFREE SOLUTION 0.8N IN H_2SO_4
$(Fe^{+2}) = 3.5 \times 10^{-5}$ M
DOSE RATE $= 8.5 \times 10^{16}$ eV/Hr/ml
Fe^{+2} IONS OXIDIZED/ml
$12^{\times 10^{15}}$
10
8
6
4
2
ENERGY ABSORBED eV/ml
1
2
3
4
5
6
7
$8^{\times 10^{17}}$

FIGURE XXVI

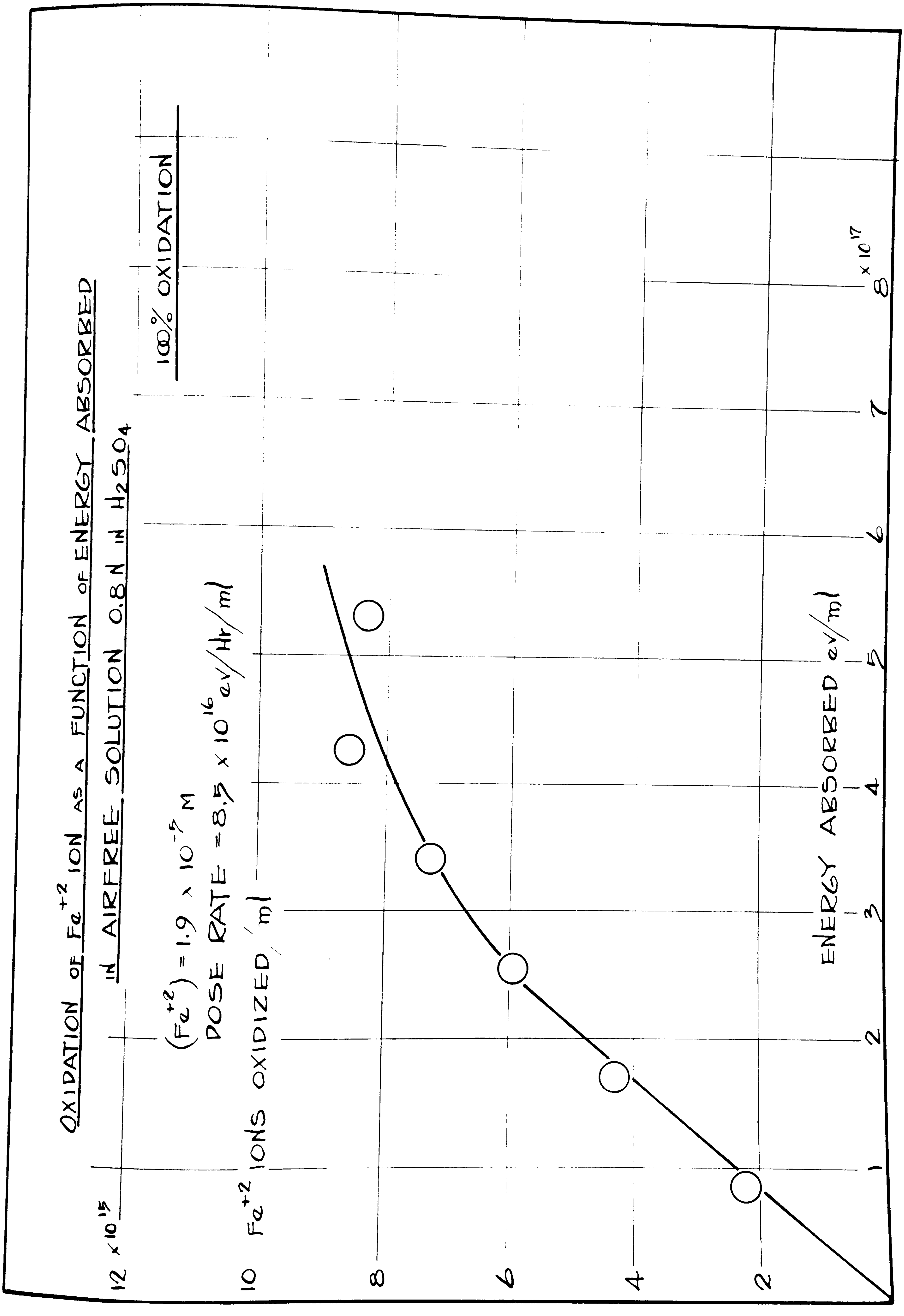


FIGURE XXVII

TABLE XXIII

Initial Oxidation Yield as a Function of Initial Fe^{+2} Ion Concentration in Airfree 0.8 N Sulfuric Acid

Dose Rate = 8.5×10^{16} ev/Hr/ml

Initial (Fe^{+2}) moles/liter	Initial Yield Fe^{+2} ions oxidized/100 ev
1.0×10^{-3}	5.2
1.0×10^{-4}	5.1
7.0×10^{-5}	3.8
4.7×10^{-5}	2.5
4.4×10^{-5}	2.1
3.5×10^{-5}	1.9
1.9×10^{-5}	2.2
1.0×10^{-5}	2.0

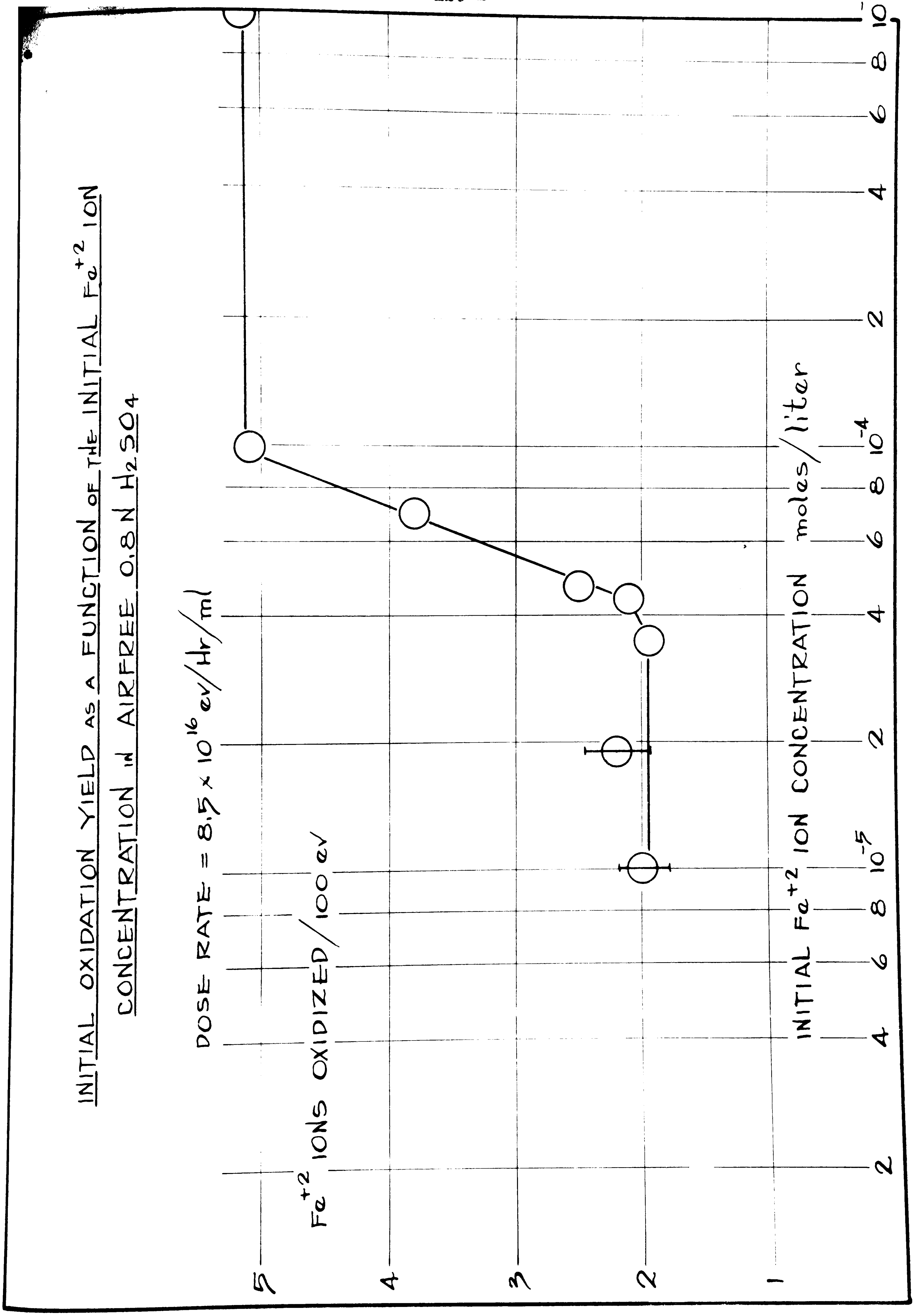


FIGURE XXVIII

Effect of Fe^{+3} Ion on Fe^{+2} Ion Oxidation in 0.8 N H_2SO_4

The oxidation of Fe^{+2} ion in airfree solution was found to be a linear function of the energy absorbed to approximately 50% oxidation. The departure from linearity above 50% oxidation suggested the possible participation of a back reaction. A back reaction that might be responsible for this effect could be reduction of Fe^{+3} ions. To test this, a Fe^{+2} ion solution (10^{-4} M) containing an equivalent concentration of Fe^{+3} ion was irradiated. The results given in Table XXIV and Fig. XXIX show that the presence of Fe^{+3} ion had no detectable effect on the oxidation of Fe^{+2} ion. This indicated that Fe^{+3} ion in airfree solution could not be reduced. This has, in fact, been observed experimentally for a Fe^{+3} solution (10^{-4} M), 0.8 N in H_2SO_4.

TABLE XXIV

Effect of Fe^{+3} Ion on Fe^{+2} Ion Oxidation in Airfree Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

$(Fe^{+3}) = 1.0 \times 10^{-4}$ M

Dose Rate = 8.3×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	Δ (Fe^{+2}) ions/ml
1.7×10^{17}	10.0×10^{15}
2.5	12.5
3.3	17.1
5.0	25.0
6.7	30.2
10.0	38.5
13.5	42.2
20.5	49.2

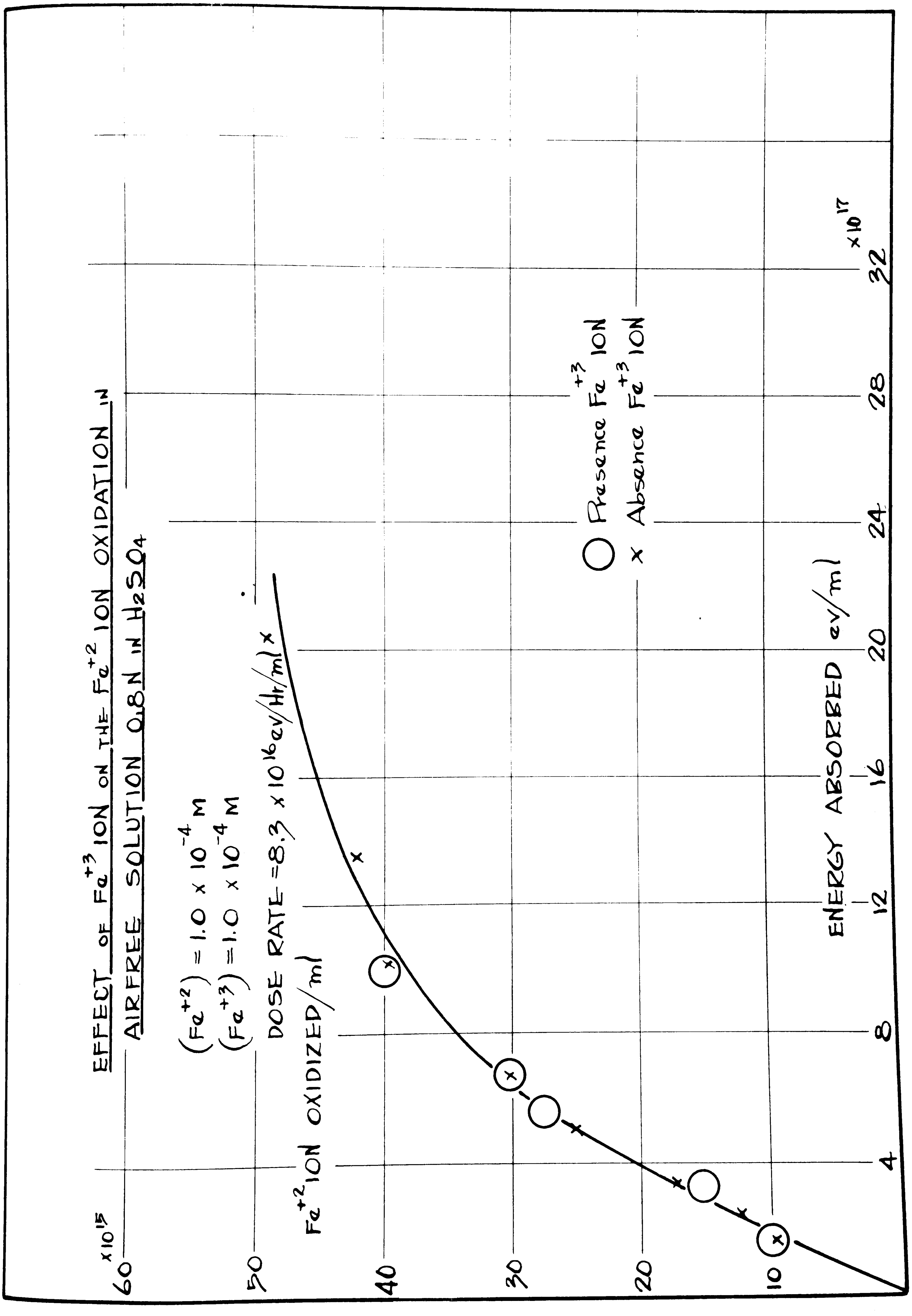
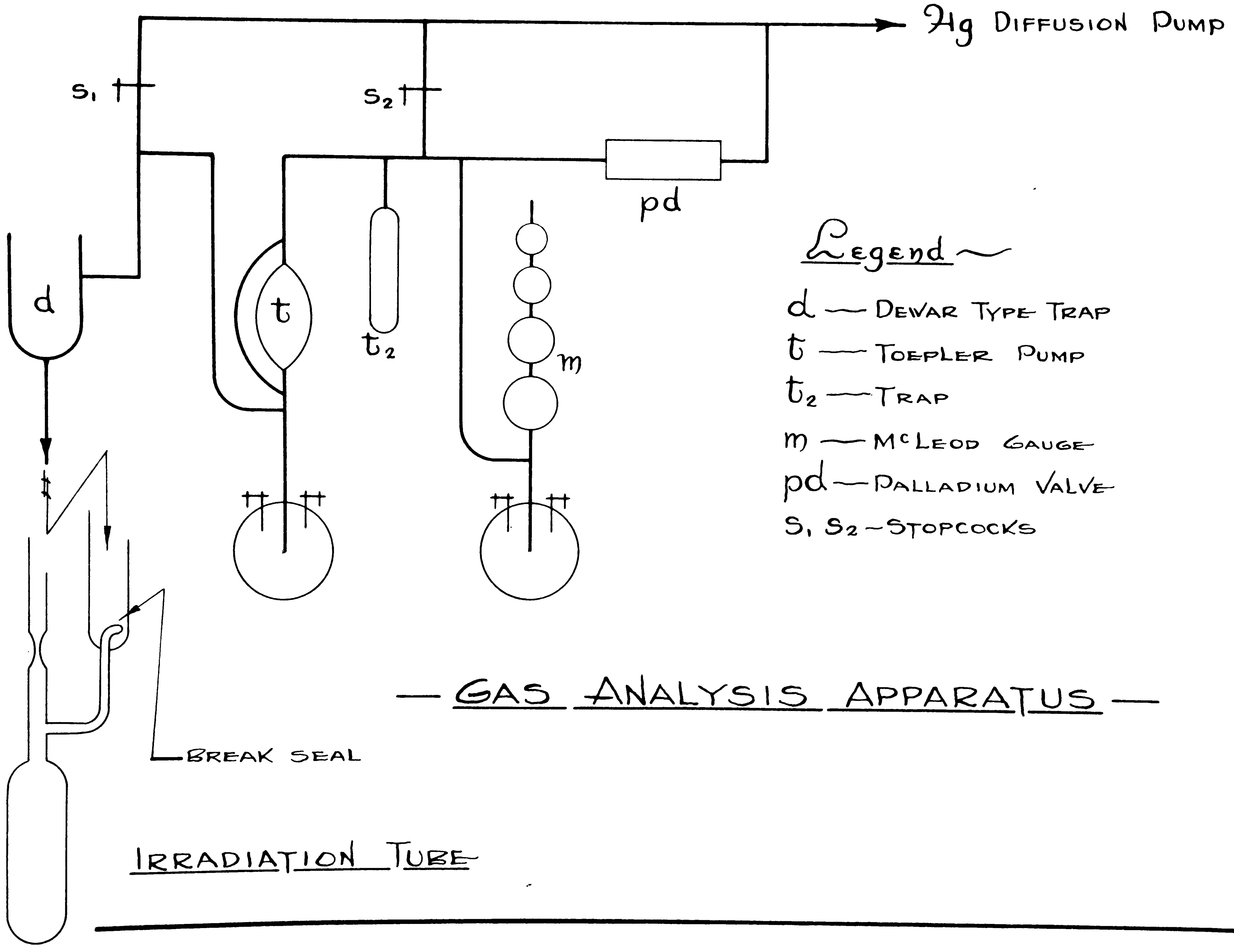

EFFECT OF Fe^{+3} ION ON THE Fe^{+2} ION OXIDATION IN
AIRFREE SOLUTION 0.8N IN H$_2$SO$_4$
(Fe^{+2}) = 1.0 x 10^{-4} M
(Fe^{+3}) = 1.0 x 10^{-4} M
DOSE RATE = 8.3 x 10^{16} ev/Hr/ml
○ Presence Fe^{+3} ION
x Absence Fe^{+3} ION
Fe^{+2} ION OXIDIZED/ml
x10^{15}
10
20
30
40
50
60
ENERGY ABSORBED ev/ml
4
8
12
16
20
24
28
32
x10^{17}

FIGURE XXIX

Formation of H_2 Gas in Airfree Fe^{+2} Solution, 0.8 N in H_2SO_4

The production of gas in airfree solutions was determined with the apparatus shown in Fig. XXX which was designed by Mr. F. H. Krenz. The special irradiation tubes used in this study are also shown. Six such irradiation tubes were constructed of almost identical dimensions and were sealed to the monster for deaeration as previously described. After irradiation, the tube was sealed to the vacuum gas analysis line as indicated in Fig. XXX, and the whole system thoroughly evacuated to a pressure less than 10^{-4} mm. Hg (limit of McLeod gauge). With a dry ice-acetone slush in trap d, the sample was opened by dropping a magnetic hammer on the break seal. The gas was transferred by the Toepler pump, t, into the McLeod gauge, m, and the total pressure measured. This was repeated several times until the pressure remained constant, after which the Hg was raised in the Toepler pump to a calibrated level. The volume of the McLeod gauge system, i.e., the system bounded by the Toepler pump, palladium valve and stopcock s_2, had been previously calibrated. A dry ice-acetone dewar was placed around trap t_2 and the pressure again measured; this was repeated with a liquid nitrogen dewar around the trap. Finally the palladium valve was turned on and the gas pressure measured periodically until it remained constant.

It was found that successively placing a dry ice-acetone and then a liquid nitrogen dewar around trap t_2 did not cause any change in the pressure. When the palladium valve was turned on, the pressure gradually fell to less than 10^{-4} mm. Hg. It may be concluded from these measurements that all the gas produced in the irradiated solutions was hydrogen. The results of this experiment are given in Table XXV and Fig. XXXI. In this figure the formation of hydrogen gas is compared with the oxidation of Fe^{+2} ion. In spite of the scarcity of points for the hydrogen formation curve, a tangent drawn to the initial part of the curve shows that the number of molecules of hydrogen formed is approximately one-half the number of Fe^{+2} ions oxidized.



— GAS ANALYSIS APPARATUS —

FIGURE XXX

TABLE XXV

Formation of H_2 Gas in Airfree Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

Dose Rate = 8.3×10^{16} ev/Hr/ml

Energy Absorbed ev/ml	H_2 Formed molecules/ml
3.3×10^{17}	9.5×10^{15}
5.9	13.6
14.5	24.6
19.9	29.4
39.8	38.4

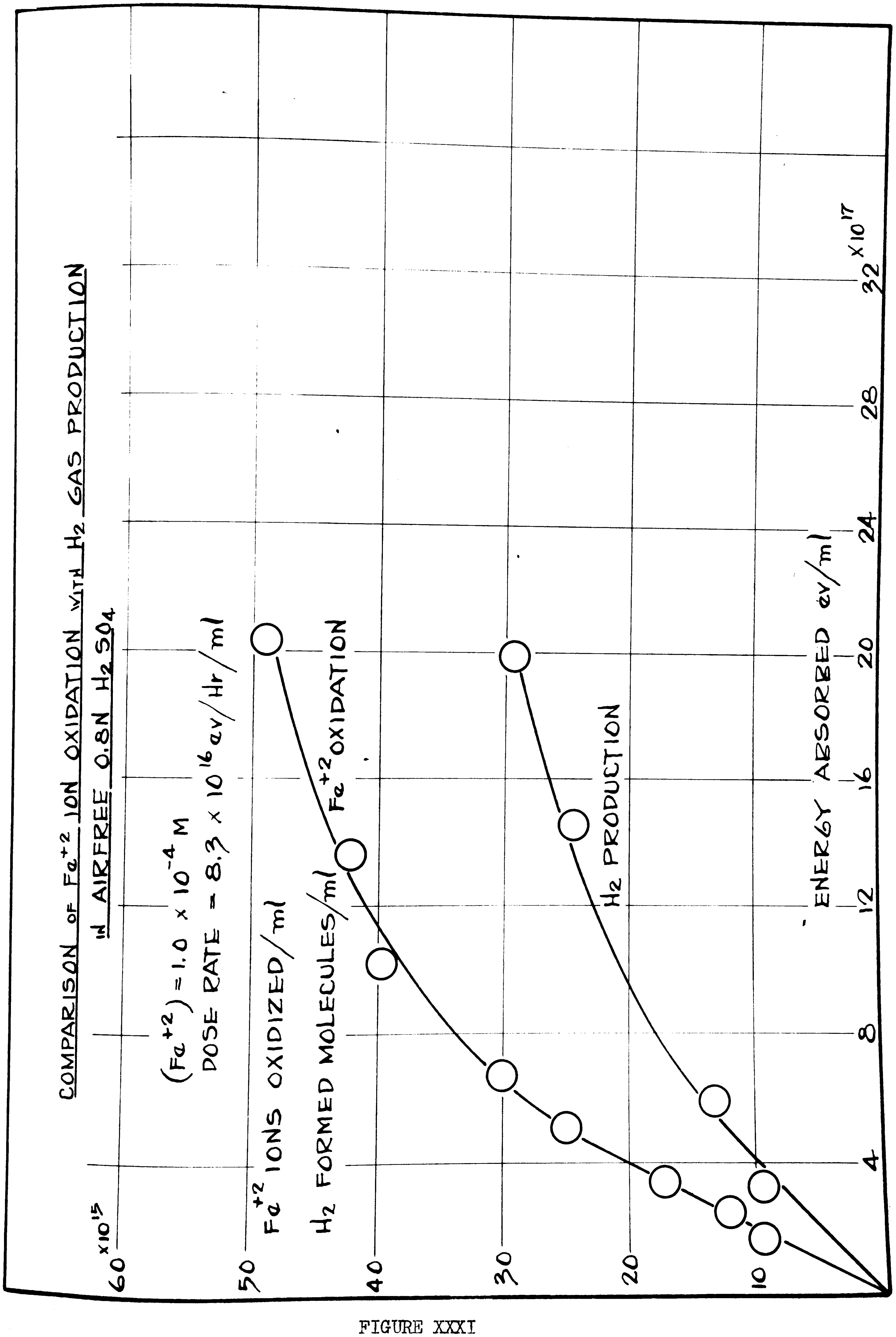

COMPARISON OF Fe+2 ION OXIDATION WITH H2 GAS PRODUCTION
IN AIRFREE 0.8N H2SO4
(Fe+2) = 1.0 x 10-4 M
DOSE RATE = 8.3 x 10^16 ev/Hr/ml
Fe+2 IONS OXIDIZED/ml
H2 FORMED MOLECULES/ml
x10^15
60
50
40
30
20
10
Fe+2 OXIDATION
H2 PRODUCTION
ENERGY ABSORBED ev/ml
4
8
12
16
20
24
28
32 x10^17

FIGURE XXXI

Effect of Temperature on Oxidation Yield in 0.8 N H_2SO_4

The effect of temperature on the oxidation of Fe^{+2} ion in airfree solution was determined with the apparatus described in part A. The solutions were heated at the required temperature for 30 minutes prior to irradiation. Six samples were deaerated as described above, and two samples were irradiated at each temperature studied, 25^o, 35^o and 45^oC for a given energy absorbed. Duplicate determinations were made at each temperature. The results are recorded in Table XXVI which show a small positive temperature coefficient. Control experiments showed negligible oxidation during the time of these experiments.

TABLE XXVI

Effect of Temperature on Oxidation Yield in Airfree Solution, 0.8 N in Sulfuric Acid

$(Fe^{+2}) = 2 \times 10^{-4}$ M

Dose Rate = 3.0×10^{16} ev/Hr/ml

Total Energy Absorbed = 2.4×10^{17} ev/ml

Temperature °C	1/T °K-1	Initial Oxidation Yield Fe^{+2} ions oxidized/100 ev
25	3.36×10^{-3}	5.2
35	3.24	6.6
45	3.14	7.8

Effect of Acid Concentration on the Oxidation of Fe^{+2} Ion

The effect of acid concentration on the oxidation of Fe^{+2} ion in airfree solution was studied at 0.8 N, 0.1 N, 0.008 N and 0.0008 N H_2SO_4, at a Fe^{+2} ion concentration of 1×10^{-4} M. The results are given in Table XXVII and Fig. XXXII, from which it can be seen that although a decrease in the acid concentration causes a decrease in the initial oxidation yield, the number of Fe^{+2} ions oxidized initially is still a linear function of the energy absorbed. It can also be seen from these results that the decrease between 0.008 N and 0.0008 N is much greater than the decrease between 0.8 N and 0.08 N. It was found that between 0.8 N and 0.1 N acid the initial oxidation yield remained unchanged.

In Table XXVIII and Fig. XXXIII are recorded the results for the effect of acid concentration on the initial oxidation yield. These results show quite clearly that the initial oxidation yield is independent of acid concentration from 0.8 N to 0.1 N. Below the latter acid concentration the yield falls off rapidly with further decrease in the acid concentration. These results are strikingly similar to those obtained in aerated solutions.

TABLE XXVII

Effect of Sulfuric Acid on Oxidation of Fe^{+2} Ion in Airfree Solution

$(Fe^{+2}) = 1.0 \times 10^{-4}$ M

Dose Rate = 8.5×10^{16} ev/Hr/ml

$(H_2SO_4) = 8 \times 10^{-3}$ N		$(H_2SO_4) = 8 \times 10^{-4}$ N	
Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml	Energy Absorbed ev/ml	$\Delta(Fe^{+2})$ ions/ml
1.7×10^{17}	4.1×10^{15}	4.9×10^{17}	3.5×10^{15}
3.4	8.5	6.2	4.0
5.1	11.5	13.6	8.1
6.8	13.9	15.1	9.5
14.0	25.1	19.8	10.8
20.4	29.0	20.6	11.5
39.6	38.5	33.5	15.5
74.5	49.0	39.6	18.9
		59.5	24.9
		79.5	30.4

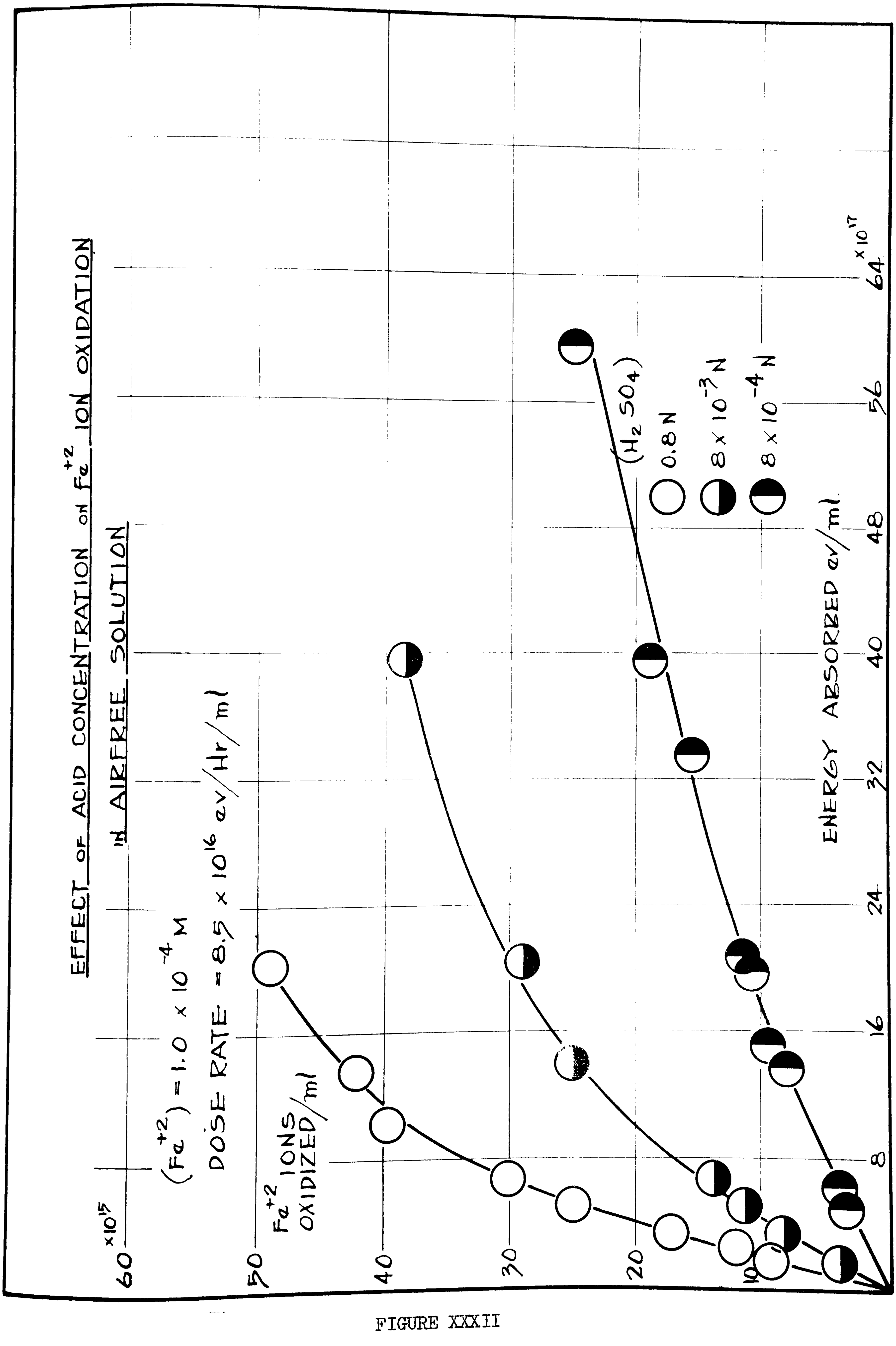


FIGURE XXXII

TABLE XXVIII

Initial Oxidation Yield as a Function of (H_2SO_4) in Airfree Solution

(Fe^{+2}) = 1.0 x 10^{-4} M

Dose Rate = 8.5 x 10^{17} ev/Hr/ml

(H_2SO_4) normal	Initial Yield Fe^{+2} ions oxidized/100 ev
8 x 10^{-1}	5.2
1 x 10^{-1}	5.1
8 x 10^{-3}	2.4
8 x 10^{-4}	0.5

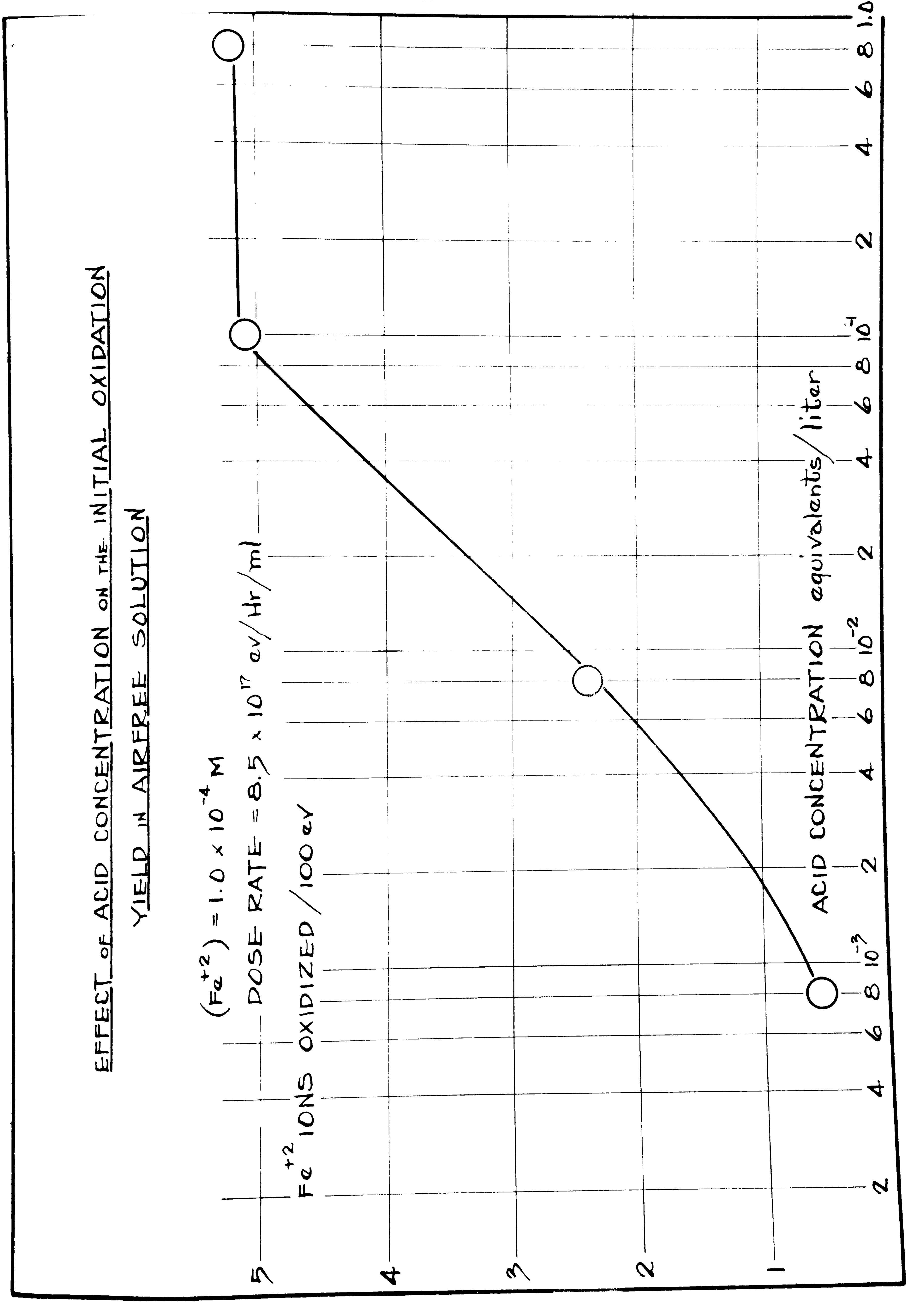


FIGURE XXXIII

DISCUSSION

The results of this investigation have shown that the γ-ray induced oxidation of Fe^{+2} ion in dilute aqueous solution is an indirect effect, both in aerated and deaerated solution. This was shown by the fact that the initial oxidation yield was independent of the initial Fe^{+2} ion concentration from 10^{-2} M to 10^{-4} M (Figs. IX and XXVIII), and that in this region the magnitude of the oxidation was a function only of the total energy absorbed by the solution (Figs. III and XXII). These results would indicate therefore, that the energy absorbed from the γ-radiation is absorbed entirely by the water. Such absorption of energy by water appears to lead ultimately to the formation of H atoms and OH radicals (57, 58, 59, 60) and it is on this basis that interpretation of the results will be attempted. In so doing, it seems reasonable to assume that the rate of formation of free radicals would be unaffected by the presence of Fe^{+2} ions in the low concentrations used in this study.

The solutions used in this investigation were prepared with the sulfates of Fe^{+2} ion and Fe^{+3} ion and usually contained high concentrations of sulfate ion and hydrogen ion from the added sulfuric acid. Because of the great tendency for Fe^{+2} ion and particularly Fe^{+3} ion to form ion association complexes with anions (e.g., CN^-, OH^-, Cl^-) it is likely that they also form complexes with sulfate ions. It would be expected therefore, that the solutions contained little if any free hydrated Fe^{+2} ion or Fe^{+3} ion. A systematic study of the sulfate complexes of Fe^{+2} ion and Fe^{+3} ion has not as yet been reported in the literature, and in the absence of any data concerning the equilibrium constants for the formation of the various possible sulfate complexes, it is difficult to ascertain the proportion and type of sulfate complex present in the solution. Furthermore, it is not known whether such complex ion formation hinders or aids the process of electron transfer to or from the ion.

Airfree Solution

In airfree solution it has been found that the initial oxidation yield is independent of the initial Fe^{+2} ion concentration between 10^{-3} M and 10^{-4} M, in 0.8 N H_2SO_4 (Fig. XXVIII). This result is in accord with the view that the chemical changes produced can be attributed to ionization and excitation of the water molecules with the resultant formation of H atoms and OH radicals. The oxidation of Fe^{+2} ion in airfree solution (in the range 10^{-3} M to 10^{-4} M) may then be attributed to the reaction,

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^-.$$

The H atoms formed in the primary process evidently recombine in pairs to form H_2 gas, since it has been found that the number of equivalents of Fe^{+2} ion oxidized is approximately equal to the number of equivalents of H_2 gas formed (Fig. XXXI) (46). Therefore, the H atoms probably disappear by the reaction,

$$H + H \longrightarrow H_2.$$

Throughout the region of concentration independence the individual oxidation-energy absorbed curves are initially linear, but above 50% oxidation they fall off, apparently toward an equilibrium state (Figs. XXII to XXVII inclusive). Such behaviour is indicative of a back reaction. Two possibilities which may explain the departure from linearity are (i) the reaction product Fe^{+3} ion is being reduced by H atoms, and (ii) the reaction product H_2 competes with Fe^{+2} ion for the available OH radicals. Explanation (i) appears to be ruled out since it was found that the addition of a large excess of Fe^{+3} ion to the Fe^{+2} ion solution, prior to irradiation, had no detectable effect on the oxidation-energy absorbed curves (Fig. XXIX). Furthermore, it was observed that an airfree Fe^{+3} ion solution (2×10^{-4} M) was not reduced in 0.8 N H_2SO_4. On the other hand, removal of OH radicals by H_2 molecules dissolved in the solution appears probable since (i) H_2 gas is known to be a reaction product and (ii) this reaction is known in the gas phase where it has an activation energy of approximately 12 kcal (75). In addition, it was observed that the H_2 gas formation decreases and tends to an equilibrium amount at the same value of the energy absorbed as the Fe^{+2} ion oxidation decreases and tends to an equilibrium value (Fig. XXXI). Hence, the tendency towards equilibrium in the oxidation may possibly be attributed to (ii), i.e., the reaction,

$$H_2 + OH \longrightarrow H_2O + H.$$

Since this reaction effectively increases the H atom concentration, and since qualitative experiments have shown that the irradiation of a Fe^{+3} ion solution, 0.8 N in H_2SO_4, containing an atmosphere of H_2 gas, results in 10 to 20% reduction, it may well be that under these conditions some Fe^{+3} ions are also reduced.

It has been found that below an initial Fe^{+2} ion concentration of 10^{-4} M, the initial oxidation yield decreases rapidly and again appears to become independent of the Fe^{+2} ion concentration at 4 x 10^{-5} M (Fig. XXVIII). Yet, throughout this region, the number of Fe^{+2} ions oxidized appears to be a linear function of the energy absorbed to approximately 50% oxidation (Figs. XXIV to XXVII inclusive). It is generally believed that a decrease in the yield at very low concentrations of the solute can be accounted for by recombination of the radicals (58). Such recombination processes would lead to the formation of H_2O, H_2 and H_2O_2, the first two of which would be inactive towards Fe^{+2} ions, whereas H_2O_2 is known to oxidize Fe^{+2} ions (77, 78). It is unlikely that recombination of an H atom with an OH radical occurs to any appreciable extent because then it would be difficult to interpret the initially linear oxidation of Fe^{+2} ion. Recombination of the radicals in pairs, i.e., giving H_2 and H_2O_2, should cause no reduction in the H_2 gas yield, and no change in the oxidation yield since one molecule of H_2O_2 will oxidize two Fe^{+2} ions which would have been oxidized had recombination not occurred. It is, however, of interest to note that at these low concentrations of Fe^{+2} ion ($< 10^{-4}$ M) the rate constant for removal of Fe^{+2} ion by H_2O_2 would indicate a half-life of several minutes for this reaction (65). Hence, it might be expected that H_2O_2 would accumulate in the solution and its presence be detected by rapid analysis of the irradiated solution, whereas experiment has shown that H_2O_2 does not accumulate in airfree Fe^{+2} solutions. This might indicate that hydroxyl radicals do not recombine to form H_2O_2 at these low concentrations of Fe^{+2} ion, or alternatively, that any H_2O_2 formed is subject to rapid decomposition by H atoms. This decomposition may occur in two ways, as follows:

$$H_2O_2 + H \longrightarrow H_2 + HO_2 \qquad \text{(i)}$$

$$\longrightarrow H_2O + OH \qquad \text{(ii)}$$

If reaction (i) were the mode of decomposition it would be expected that the solution would gradually become oxygenated with a resultant increase in the oxidation yield. This has never been observed. Moreover, a consideration of the $H-HO_2$ bond strength (70 - 100 kcal.) (68,90) and that of the O-O bond strength in H_2O_2 ($\sim$ 35 kcal.) (91) strongly indicates that decomposition occurs via reaction (ii). The fate of the OH radical produced in this reaction may be,

$$OH + H_2 \longrightarrow H_2O + H \qquad \text{(iii)}$$

Thus, it is seen that reactions (ii) and (iii) constitute a simple chain decomposition of H_2 and H_2O_2. This chain sequence was originally proposed by Allen (59) to account for the very low, barely detectable, steady state concentration of H_2O_2 produced by electron bombardment of airfree water. It would be of interest to study the yield of H_2 gas as a function of the initial Fe^{+2} ion concentration from 10^{-4} M to 10^{-5} M.

It should be emphasized that below an initial Fe^{+2} ion concentration of 10^{-4} M, the initial oxidation yield falls rapidly but apparently again becomes independent of the Fe^{+2} ion concentration at concentrations below 4×10^{-5} M (Fig. XXVIII). If the decrease in the oxidation yield were due to recombination of hydroxyl radicals, it is difficult to see why the oxidation yield should again become independent of the Fe^{+2} ion concentration, since recombination of hydroxyl radicals would be expected to increase with further decrease in the Fe^{+2} ion concentration and consequently the oxidation yield would eventually tend to zero. It is of interest, however, to consider the possibility that dimerization of OH radicals might occur independently of the Fe^{+2} ion concentration. This does not appear improbable if the physical process is considered whereby the OH radicals are formed in water. It is known from studies in the gas phase, that as a fast electron dissipates its energy in an absorbing medium, the specific ionization increases and attains a maximum as the electron comes to rest. Since the hydroxyl radicals will be formed in the track of the fast electron, it is reasonable to assume that the radical concentration per unit length of track increases as the velocity of the electron decreases. It may be further assumed that in the region of high radical concentration (i.e., in the regions near the ends of electron tracks) the conditions are most favourable for dimerization of hydroxyl radicals. On this view, then, the oxidants present in airfree solution would be OH radicals and H_2O_2 molecules, both of which oxidize Fe^{+2} ions. It has been noted that at Fe^{+2} ion concentrations of less than 10^{-4} M, the reaction between Fe^{+2} ion and H_2O_2 would have a half-life of several minutes, and it may be that the decrease in yield might be attributed to inefficiency in this reaction. The appearance of a region of concentration independence at concentrations below 4×10^{-5} M might indicate that the H_2O_2 formed by dimerization of hydroxyl radicals is no longer contributing to the Fe^{+2} ion oxidation, since it is being removed in the chain sequence (ii) and (iii).

From the preceding discussion it appears reasonable that the decrease in the oxidation yield is probably due to the recombination of the hydroxyl radicals, whether this occurs independently of the Fe^{+2} ion concentration or not. It is difficult from the available data to find a completely satisfactory explanation for the decrease in the oxidation yield below 10^{-4} M Fe^{+2} ion in airfree solution.

The kinetics of the indirect oxidation of Fe^{+2} ion in the region of concentration independence (concentrations of Fe^{+2} ion greater than 10^{-4} M) may be readily accounted for if it is assumed that the only oxidant formed is the hydroxyl radical. From the following sequence of reactions an expression is derived which appears to account for the experimental results.

$$H_2O \xrightarrow{\gamma} H + OH$$

$$Fe^{+2} + OH \xrightarrow{k_1} Fe^{+3} + OH^- \qquad (1)$$

$$H + H \longrightarrow H_2 \qquad (2)$$

$$H_2 + OH \xrightarrow{k_3} H_2O + H \qquad (3)$$

If k_1 and k_3 are the rate constants for the removal of OH radicals by Fe^{+2} ion and H_2 respectively, and if I is the rate of energy absorption and k a proportionality constant, then the rate of formation of OH radicals will be given by:

$$\frac{d(OH)}{dt} = kI - k_1(Fe^{+2})(OH) - k_3(H_2)(OH)$$

If it is assumed that the OH radicals are formed uniformly throughout the irradiated solution, then it is possible to apply steady state conditions to this equation, from which

$$\frac{d(OH)}{dt} = 0$$

and $$(OH) = \frac{kI}{k_1(Fe^{+2}) + k_3(H_2)}$$

Now, the rate of disappearance of Fe^{+2} ion will be given by,

$$-\frac{d(Fe^{+2})}{dt} = k_1(Fe^{+2})(OH)$$

and substitution of the above value for (OH) gives,

$$-\frac{d(Fe^{+2})}{dt} = \frac{kI.k_1(Fe^{+2})}{k_1(Fe^{+2}) + k_3(H_2)}$$

This equation can be reduced to,

$$-\frac{d(Fe^{+2})}{dt} = \frac{kI}{1 + \frac{k_3(H_2)}{k_1(Fe^{+2})}} \qquad (A)$$

If it is further assumed that $1 \gg k_3(H_2)/k_1(Fe^{+2})$, i.e., that $k_1(Fe^{+2}) \gg k_3(H_2)$, then

$$-\frac{d(Fe^{+2})}{dt} = kI \qquad (B)$$

This equation indicates that when essentially all the OH radicals are removed by reaction with Fe^{+2} ions, i.e., at sufficiently high Fe^{+2} ion concentrations, the oxidation will be a linear function of the energy absorbed.

Equation (A) indicates that when reaction (3) becomes important, i.e., at sufficiently low Fe^{+2} ion concentrations, the rate of oxidation will gradually decrease. When $k_3(H_2) \gg k_1(Fe^{+2})$, then

$$-\frac{d(Fe^{+2})}{dt} = kI\frac{k_1}{k_3}\frac{(Fe^{+2})}{(H_2)}$$

A successful evaluation of all the implications of this equation can only be made by a thorough study of the initial oxidation yield as a function of the H_2 concentration in the solution.

The mechanism proposed above to account for the oxidation of Fe^{+2} ions indicates that the oxidation yield should be independent of the acid concentration. This is partially in agreement with experiment, i.e., for acid concentrations from 0.8 N to 0.1 N. However, it has been observed that below 0.1 N acid concentration, the initial oxidation yield decreases rapidly with decrease in the acid concentration (Fig. XXXIII). Recently Amphlett (88) has proposed that the pH effect in the oxidation of Fe^{+2} ion may be due partially to a mechanism which does not involve hydrogen ions, but depends on the stability and reactivity of certain complexes. It is known that the Fe^{+2} ion readily associates with OH^- ions to form the complex $FeOH^{+2}$ (89). From a study of the γ-ray induced oxidation of $Fe(ClO_4)_2$ in $HClO_4$ solutions, Amphlett has found that the ratio $(Fe^{+3})/(Fe^{+2})$ increases as the acid concentration is increased. These results appear to be comparable with those obtained in sulfate solutions. Amphlett suggests that, for $HClO_4$ solutions, the increased formation of Fe^{+3} ion with increase in the acid concentration may be attributed to the equilibrium,

$$Fe^{+3} \rightleftharpoons FeOH^{+2} + H^+.$$

His interpretation, of course, implies that Fe^{+3} ion is much more resistant to reduction by H atoms than is $FeOH^{+2}$. In sulfate solutions this scheme will be complicated by the complexing of the Fe^{+2} and Fe^{+3} ions by sulfate and possibly bisulfate ions.

To account for the pH effects observed in many radiation induced chemical changes in aqueous solution, Weiss (87) has recently suggested that H atoms in solution are in equilibrium with H_2^+ ions as follows,

$$H + H^+ \rightleftharpoons H_2^+.$$

If such equilibrium exists, it is evident that a reducing entity (H atom) has been converted to an oxidizing entity (H_2^+ ion) which can probably oxidize Fe^{+2} ion as follows,

$$Fe^{+2} + H_2^+ \longrightarrow Fe^{+3} + H_2.$$

At high acid concentrations it is apparent that both OH and H_2^+ can oxidize Fe^{+2} ions, whence the equivalence between the Fe^{+2} ions oxidized and H_2 gas formed would be maintained. At lower acid concentrations, the above equilibrium would be shifted to the left with a resultant decrease in the oxidation. It is not evident, however, that such a suggestion can also account for a similar pH effect observed in aerated solution.

The effect of temperature on the initial oxidation yield has indicated a small but measurable temperature coefficient (Table XXVI). Because of the complexity of the mechanism it is doubtful whether the temperature coefficient can be related to any specific reaction. It may be significant however, that the activation energy which can be calculated from the temperature coefficient is of the same order of magnitude as the activation energy for diffusion in aqueous solution (76). It might be that an increase in temperature increases the number of radicals which are able to diffuse out of the electron track before recombination of H and OH can occur, but it is also possible that the temperature effect can be attributed to some equilibrium process in the system.

Aerated Solution

In aerated solution it has been found that the oxidation yield is independent of the initial Fe^{+2} ion concentration over a very wide range, which suggests that the γ-ray energy is absorbed entirely by the water. According to the recent proposal of Weiss (57), the absorption of high energy radiation in water results in the formation of H atoms and OH radicals. It is generally agreed that in the presence of oxygen dissolved in water, the conversion of an H atom into an HO_2 radical can explain many features of the decomposition of aerated water by X- and γ-rays (59). In the interpretation of the results of the present investigation, it will be assumed that all the H atoms formed in the primary act are rapidly converted to an HO_2 radical, i.e., an originally reducing entity is converted to an oxidizing entity. Therefore, in aerated solutions, it may be considered that the primary radicals are OH and HO_2 produced by the following reactions,

$$H_2O \xrightarrow{\gamma} H + OH \qquad (1)$$

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

The oxidation of Fe^{+2} ions by these oxidants may proceed as follows,

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^- \qquad (3)$$

$$Fe^{+2} + HO_2 \longrightarrow Fe^{+3} + HO_2^- \qquad (4)$$

Since the solutions usually contained high concentrations of acid, the equilibrium,

$$H^+ + HO_2^- \rightleftharpoons H_2O_2 \qquad (5)$$

can contribute to the oxidation by the reaction,

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH. \qquad (6)$$

Reactions (3), (4), (5) and (6) as here written were originally proposed by Haber and Weiss (77) to account for their results on the catalytic decomposition of H_2O_2 by iron salts.

Inspection of reactions (1) to (6) indicates that for every free radical pair produced in the primary process, four Fe^{+2} ions are oxidized and one oxygen molecule consumed. It would be expected, therefore, that the oxidation yield in aerated solution would be four times greater than in airfree solution. This is borne out by the experiments outlined previously. It should also be noted that H_2 gas would not be formed in aerated solutions, and this has, in fact, been observed by Fricke (46).

The zero order kinetics observed in the region of concentration independence suggest that the rate determining step is independent of the Fe^{+2} ion concentration and must therefore depend only on the rate of radical formation, in the absence of any complicating effects. Consequently, reactions (3), (4) and (6) must be very rapid in comparison with the rate of radical formation. On the basis of the above reactions, a preliminary kinetic analysis may be made using the Bodenstein approximation, i.e., assuming steady state conditions for the intermediates. If k_3, k_4 and k_6 are the rate constants for removal of the oxidants OH, HO_2 and H_2O_2 respectively by Fe^{+2} ions and I is the rate of energy absorption and k a proportionality constant, then the rate of formation of oxidants will be given as follows,

$$\frac{d(OH)}{dt} = kI - k_3(Fe^{+2})(OH) + k_6(Fe^{+2})(H_2O_2) = 0$$

$$\frac{d(HO_2)}{dt} = kI - k_4(Fe^{+2})(HO_2) = 0$$

$$\frac{d(H_2O_2)}{dt} = k_4(Fe^{+2})(HO_2) - k_6(Fe^{+2})(H_2O_2) = 0$$

From these equations the concentration of the intermediate oxidants are,

$$(OH) = \frac{kI + k_6(Fe^{+2})(H_2O_2)}{k_3(Fe^{+2})} = \frac{2kI}{k_3(Fe^{+2})}$$

$$(HO_2) = \frac{kI}{k_4(Fe^{+2})}$$

$$(H_2O_2) = \frac{k_4(Fe^{+2})(HO_2)}{k_6(Fe^{+2})} = \frac{kI}{k_6(Fe^{+2})}$$

These equations yield the entirely reasonable conclusion that, in each case, the steady state concentration of oxidant is directly proportional to the rate of energy absorption.

The rate of oxidation of Fe^{+2} ion will be given by,

$$-\frac{d(Fe^{+2})}{dt} = k_3(Fe^{+2})(OH) + k_4(Fe^{+2})(HO_2) + k_6(Fe^{+2})(H_2O_2).$$

Substitution of the above values for (OH), (HO_2) and (H_2O_2) gives,

$$-\frac{d(Fe^{+2})}{dt} = 4kI \qquad \text{or} \qquad -\frac{d(Fe^{+2})}{Idt} = 4k \qquad (A)$$

According to equation (A) the oxidation of Fe^{+2} ion should be zero order with respect to the Fe^{+2} ion concentration and a function only of the energy absorbed. Hence, a plot of the number of Fe^{+2} ions oxidized should be a linear function of the energy absorbed. The experimental data have been found to agree well with this conclusion (Figs. II, III and IV). Furthermore, from the slope of this plot the proportionality constant k can be evaluated. This constant is the number of free radical pairs formed per electron volt and the experimental data indicate k to be 0.05, corresponding to a value of 20 ev for the amount of energy required to form a free radical pair in water. This may be compared with a value of 32.5 ev generally believed to be the amount of energy required to form an ion pair in air (62).

Equation (A) implies that the oxidation yield should be independent of the intensity throughout the region of concentration independence. This has been found to be true in the present study over a limited range of intensities (approximately two-fold) (Figs. II, III and IV). Recently, Todd and Whitcher (50) have found the oxidation yield to be independent of the intensity over a fifty-fold range. A similar intensity independence has been observed by Miller (51).

The mechanism proposed above for the oxidation of Fe^{+2} ion in aerated solution indicates that four Fe^{+2} ions are oxidized per oxygen molecule consumed. Further evidence in support of this has been obtained by Fricke and Morse (44) and more recently by Miller (51). Starting with an initially air saturated solution of Fe^{+2} ion ($\sim 2 \times 10^{-3}$ M) these authors found that when approximately 0.9×10^{-3} M had been oxidized there was a sudden break in the oxidation-energy absorbed curve. These authors assumed that the break corresponds to complete consumption of oxygen and calculated that the number of equivalents of Fe^{+2} ion oxidized is equal to the number of equivalents of oxygen consumed. It would be expected, therefore, that if all the oxygen had been consumed the oxidation yield should be that for an airfree solution. This, however, was not the case, for after the break the yield was found to be approximately 2.5 times less than the yield in the fully aerated solution. The recent work of Miller (51) has shown that with an initially oxygen saturated solution similar results are obtained except that after the break has occurred the yield has decreased by a factor of 3.3.

The individual oxidation-energy absorbed curves obtained throughout the region of concentration independence show a striking feature in that, within the experimental error, they are linear to complete oxidation (Figs. II, III and IV). This suggests that the reaction is probably uncomplicated by side reactions, and certainly indicates the absence of any gross back reaction. In this case the back reaction would be reduction of the Fe^{+3} ion, which, if it occurred, would result in the appearance of an equilibrium state in the oxidation.

It has, in fact, been found that the addition of a large excess of Fe^{+3} ion prior to the irradiation apparently leads to an equilibrium, even though the initial oxidation yield is unchanged (Fig. XI). Since the initial oxidation yield remained unchanged this would suggest that, in 0.8 N H_2SO_4, the rate constant for the reaction,

$$Fe^{+3} + HO_2 \longrightarrow Fe^{+2} + H^+ + O_2 \qquad (7)$$

is probably much smaller than that for reaction (4). Since an ion-free radical reaction such as reaction (7) might be expected to have a small activation energy, the A term in the rate equation $k = A.e^{-E/RT}$ should probably be small. Since the activated complex for this reaction probably resembles more closely the products than the reactants, then according to Eyring (76) the entropy of activation might be comparable with the difference in entropy between reactants and products. A preliminary calculation of the entropy change was made by evaluating the free energy change and the heat of reaction in the usual manner, using the data given by Latimer (79). This calculation indicated an entropy change of about -180 E.U. at 25°C for reaction (7), which suggests that the A term in the rate equation is probably very small. If it is assumed that the energies of activation for reactions (4) and (7) are very small, then from the ratio $(Fe^{+3})/(Fe^{+2})$ at which departure from linearity in the presence of added Fe^{+3} ion occurs, and a knowledge of the A term for reaction (4) (65), it is possible to determine an upper value for the A term in reaction (7). The value obtained is 5×10^7.

The inclusion of reaction (7) implies that in the absence of added Fe^{+3} ion, the oxidation should not be linear to 100%. It is evident, however, that this effect would be observed in the last 4 or 5% of the oxidation and consequently would be difficult to test experimentally. According to reaction (7) it would be expected that aerated Fe^{+3} ion solutions would be reduced. This, however, has never been observed when the solutions contained 0.8 N H_2SO_4.

A study of the effect of temperature on the oxidation of Fe^{+2} ion has indicated a very small positive temperature coefficient (Table X). It is interesting to note that the temperature coefficient observed here is similar to that calculated from the data of Bonet-Maury and Lefort (35) for the formation of H_2O_2 in aerated water irradiated with X-rays. Because of the complexity of the mechanism, it is not feasible with the present data to account satisfactorily for the temperature coefficient in the oxidation of Fe^{+2} ion.

It has been found that below an initial Fe^{+2} ion concentration of 10^{-4} M the initial oxidation yield decreased (Fig. IX). This decrease in yield at very low solute concentrations is generally attributed to recombination of the primary free radicals (58). Presumably, then, the oxidation would not be a linear function of the energy absorbed to 100% oxidation at an initial Fe^{+2} ion concentration of 10^{-4} M. This, however, is contrary to experiment (Fig. IV). In addition, the results have shown that for any initial Fe^{+2} ion concentration below 10^{-4} M the oxidation is always a linear function of the energy absorbed to approximately 70% oxidation (Figs. V to VIII inclusive). Thus it appears that even though the initial oxidation yield is a function of the initial Fe^{+2} ion concentration, it is apparently independent of the instantaneous Fe^{+2} ion concentration.

This rather anomalous feature is difficult to interpret in terms of free radical recombination.

The linear oxidation with energy absorbed at Fe^{+2} ion concentrations below 10^{-4} M suggest that some oxidant is formed which may account for this effect. It has been found, in the region of concentration dependence, that some oxidant, assumed to be H_2O_2, does, in fact, accumulate in the irradiated solution (Figs. XVII, XVIII and XIX). The accumulation of this oxidant was found to be inversely proportional to the intensity of irradiation (Fig. XX). This might be expected, since a decrease in the intensity would increase the time necessary to accumulate a given amount of H_2O_2 in the solution. Hence, this would lead to a decrease in the H_2O_2 accumulated because of the longer time that the Fe^{+2} ion could react with the H_2O_2. At these low concentrations of Fe^{+2} ion ($< 10^{-4}$ M) the rate constant for the removal of Fe^{+2} ion by H_2O_2 indicates a half-life of several minutes for this reaction (65). Furthermore, it was observed that the accumulation of H_2O_2 in the solution would exactly account for the decrease in the oxidation yield. Hence, it is evident that the decrease in the oxidation yield below an initial Fe^{+2} ion concentration of 10^{-4} M can probably be accounted for by inefficiency in the Fe^{+2} - H_2O_2 reaction.

Qualitatively the accumulation of H_2O_2 in the solutions appears to account for the linear oxidation at these low concentrations. This appears reasonable since the oxidation curve and the H_2O_2 accumulation curve are of exactly the same shape (Figs. XVII, XVIII and XIX). These curves also indicate that the last 30% of the oxidation is due entirely to oxidation by H_2O_2, which has attained a steady state concentration.

In this region the oxidation is approximately first order with respect to the Fe^{+2} ion concentration.

Further evidence in favour of the above interpretation of the decrease in the oxidation yield may be cited. First, it has been observed that heating an irradiated solution of concentration greater than 10^{-4} M Fe^{+2} ion had no effect. Second, the addition of H_2O_2 to a solution of Fe^{+2} ion concentration greater than 10^{-4} M causes rapid oxidation of the Fe^{+2} ion.

In reactions (4) and (7) it is assumed that the HO_2 radical can act both as an oxidizing agent as well as a reducing agent. This dual character of the HO_2 radical was originally suggested by Haber and Weiss (77). More recently, Baxendale and co-workers (78) have considered this property of the HO_2 radical to explain their results on the decomposition of H_2O_2 solutions by Fe^{+2} and Fe^{+3} ions. From their work they find that k_7/k_4 is a function of the H^+ concentration given by the relation,

$$\frac{k_7}{k_4} = \frac{K}{(H^+) + K_1}$$

They account for this relation by rewriting reaction (7) as,

$$Fe^{+3} + O_2^- \longrightarrow Fe^{+2} + O_2 \qquad (8)$$

This implies that the following equilibrium is rapidly established,

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (9)$$

Using the free energy of ionization for reaction (9) given by Latimer

(79), the equilibrium constant for this reaction is found to be of the order of 10^{-7}.

If the equilibrium in reaction (9) is rapidly established this suggests that the steady state concentration of the HO_2 radical would be directly proportional to the H^+ ion concentration. Consequently, a decrease in the H^+ ion concentration would decrease the oxidation yield. It has, in fact, been observed that for acid concentrations below 0.1 N the oxidation yield is approximately proportional to the H^+ ion concentration (Fig. XV). At a given acid concentration less than 0.1 N, it has been observed that the oxidation is initially linear but tends toward an equilibrium state (Figs. XII and XIII). The tendency toward an equilibrium indicates that the rate of Fe^{+3} ion reduction is becoming equal to the rate of Fe^{+2} ion oxidation. Initially the Fe^{+3} ion concentration is zero so that reaction (8) does not occur. Reaction (8) appears to account for the reduction of aerated Fe^{+3} ion solutions when the acid concentration is less than 0.1 N.

A second possible explanation for the effect of acid may be given based on the reverse of reaction (4), namely,

$$Fe^{+3} + HO_2^- \longrightarrow Fe^{+2} + HO_2 \qquad (10)$$

This reaction was originally proposed by Haber and Weiss (77). From equation (5) the concentration of HO_2^- ion will be given by,

$$(HO_2^-) = \frac{K(H_2O_2)}{(H^+)}$$

where K is the equilibrium constant for the ionization of H_2O_2. This equation shows that decrease in the H^+ ion concentration will increase the concentration of HO_2^- ion. This will tend to favour reaction (10), with a resultant decrease in the oxidation of Fe^{+2} ion.

It has been observed that the acid concentration has no effect on the shape of the oxidation yield-Fe^{+2} ion concentration curve (Fig. XVI). That is, even in the region where the oxidation yield is a function of the acid concentration, the yield is found to be independent of the Fe^{+2} ion concentration from 10^{-3} M to 10^{-4} M. This implies that the decrease in the oxidation yield with Fe^{+2} concentration is independent of the H^+ ion concentration.

THERMODYNAMIC CONSIDERATIONS

Some consideration has been given to the energetics of the free radical reactions mentioned in the preceding discussion. In the absence of any data pertaining to the rates of these free radical reactions here used, it was felt that preliminary calculations of the energetics of these reactions might aid considerably in elucidating the mechanism.

In pure water absorbing high energy radiation the overall primary process is generally written as,

$$H_2O \longrightarrow H + HO \qquad (a)$$

If the water is aerated, it is generally considered that the H atom would be converted into a perhydroxyl radical as follows,

$$H + O_2 + M \dashrightarrow \dot{HO_2} + M \qquad (b)$$

Therefore, in aerated water the primary radicals may be considered to be HO and HO_2, while in airfree water the primary radicals are HO and H. However, in aerated water in the presence of a solute reactive towards H atoms, but not to HO_2, it is well to remember that the formation of HO_2 will depend largely on the relative concentrations of the solute and O_2 molecules, assuming, of course, that other things are equal.

It is believed that simple association reactions, such as reaction (b) above, require the presence of a third body to remove the large heat of formation, approximately 60 - 70 kcal. The results of Bates and Cook (80) on the photo-oxidation of HI in the gas phase (pressures > 15 cm.) have shown that reaction (b) above is in fact termolecular and occurs approximately once out of every two or three collisions, which indicates a low activation energy. Rosen (81), however, has considered this problem on the basis of the quantum theory and concluded that an HO_2 radical formed in a bimolecular collision would be stabilized by conversion of the energy of formation into vibrational energy. Recently, Minkoff (82) has made a study of the potential energy surface for the reaction,

$$H + O_2 \longrightarrow HO + O$$

and concluded that HO_2 can be formed from H and O_2 with a very small activation energy. In the presence of a third body, to remove some of the energy of formation, the radical no longer possesses the requisite energy for its dissociation and it should then be stable. Furthermore, Minkoff showed that if the reactants possessed sufficient energy the system would pass from HO_2 to HO + O unless energy is removed by a third body before the system passes over the high potential barrier. It would appear, therefore, that in a condensed phase were the conditions for a three body collision of this type already present, a collision between H and O_2 will result in the formation of an HO_2 radical in the ground state.

To account for the observed decomposition products when pure water is irradiated, it is only necessary to consider various possible combination reactions involving the primary free radicals. This aspect of the radiation chemistry of water has already been considered in the introduction. However, it is interesting to consider the energetics of some of these reactions. The following reactions are of prime interest,

	ΔF kcal/mole	
$OH + HO_2 \longrightarrow H_2O + O_2$	-55	(c)
$OH + OH \longrightarrow H_2O_2$	-21	(d)
$OH + OH \longrightarrow H_2O + O$	+ 8	(e)
$HO_2 + HO_2 \dashrightarrow H_2O_2 + O_2$	-37	(f)
$HO_2 + HO_2 \longrightarrow H_2O + O_3$	-23.3	(g)

Reaction (c) is essentially recombination of the primary radicals and will in all probability have a very small activation energy. Much discussion has been centered on reactions (d) and (e), the combination of two OH radicals. Weiss (67) pointed out in 1940 that reaction (d) would have an appreciable activation energy due to the large dipole repulsion forces between two OH radicals as they approached in a configuration favourable to the formation of H_2O_2. Weiss has calculated that the activation energy due to the repulsion forces would be about 5 kcal. Further, he considers that two approaching OH radicals will assume the position of lowest potential energy, which means that oppositely charged ends of the dipoles will attract. In view of this, Weiss favours reaction (e) over reaction (d). However, it also appears important to consider the fact that in aqueous solution the OH radicals are very likely hydrated, which would tend to reduce their repulsive force. In fact, this force will have approximately 1/80 of its value in vacuo. This would therefore permit a much closer approach of two OH radicals, in which case the exchange interaction would operate to bring about strong attraction between the radicals. Furthermore, it appears that reaction (d) is favoured over reaction (e) on energetic grounds, since reaction (d) proceeds with a large decrease in free energy, while reaction (e) has a positive free energy change.

The combination of two OH radicals to form H_2O_2 will be greatly facilitated if the radicals are produced in an excited state. It is not unlikely that such a condition exists in the tracks of densely ionizing radiation (α-particles, etc.) and also at the ends of electron tracks. Experimental evidence from the heavy particle irradiation of water indicates that such a process as this does in fact occur. Furthermore, that the yield of H_2O_2 is independent of temperature, for α-particle irradiation, suggests little or no activation energy for reaction (d), or else that the requisite activation energy is already present. Apart from the fact that the radicals may be formed in excited states, it is also important to consider the spatial distribution of the radicals. Thus, with heavy particle irradiation the radicals will be produced very close together in columns, which tends to favour reaction (d), while with light particle irradiation the radicals are on the average produced with a uniform distribution, separated by several water molecules. In this case, however, the formation of H_2O_2 in aerated water by X-radiation is due largely to reaction (f). In airfree water the formation of H_2O_2 is due to reaction (d) which will take place at the ends of electron tracks. The very small steady state concentration of H_2O_2 observed is attributed to the very efficient back reaction,

$$H + H_2O_2 \longrightarrow H_2O + HO$$

Similarly, the very small steady state pressure of H_2 gas is attributed to,

$$H_2 + HO \longrightarrow H_2O + H$$

In effect, these two reactions result in the chain decomposition of the reaction products H_2O_2 and H_2 (28).

The dismutation of perhydroxyl radicals, reaction (f), is favoured by the large negative free energy change. This reaction will also be facilitated by the strong permanent dipole moment of the perhydroxyl radical. However, perhydroxyl is also unstable with respect to the decomposition into ozone and water, reaction (g). Thermodynamically, reaction (f) is the more probable of the two decompositions. It has been found experimentally that KO_2 gives an almost qualitative yield of H_2O_2 and O_2 when treated with acid (83). Furthermore, H_2O_2 is known to be a rapid catalyst for the decomposition of O_3 into O_2 (84).

The oxidation of Fe^{+2} ion in dilute aqueous solution by γ-radiation has been shown to be independent of the initial Fe^{+2} ion concentration over a wide range. That is, under the conditions of these experiments, the oxidation of Fe^{+2} ion is an indirect effect. Therefore, it was found advantageous to discuss the mechanism of this reaction in terms of the current free radical theory. Hence, the oxidation of Fe^{+2} ion in aerated solution has been attributed to the following reactions,

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^- \qquad (1)$$

$$Fe^{+2} + HO_2 \longrightarrow Fe^{+3} + HO_2^- \qquad (2)$$

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH \qquad (3)$$

These reactions were in fact originally proposed by Haber and Weiss (77) to account for their results on the catalytic decomposition of H_2O_2 by iron salts. In their mechanism, the OH radical produced in reaction (3) may react either with H_2O_2, thereby initiate the chain reaction, or else with Fe^{+2} ion, which effectively terminates the chain. The catalytic decomposition by Fe^{+3} ion has been attributed to the reverse of reaction (2), with the formation of HO_2 radical which could also initiate the chain reaction.

In view of the extreme importance of reactions (1), (2) and (3), it is interesting to consider their energetics. In the following calculations it is assumed that all oxidants are produced in their ground states. The heats of these reactions may be obtained from hypothetical cyclic processes. Thus reaction (1) may be considered to take place in the following cycle.

$$\begin{tikzcd}
Fe^{+2}_{aq} \arrow[d, "I_{Fe^{+2}}"'] & + & OH_{aq} \arrow[r, "\Delta H"] \arrow[d, "S_{OH}"'] & Fe^{+3}_{aq} & + & OH^{-}_{aq} \\
Fe^{+3}_{aq} & + e + & OH_{g} \arrow[r, "E_{OH}"] & Fe^{+3}_{aq} \arrow[u] & + & OH^{-}_{g} \arrow[u, "S_{OH^{-}}"']
\end{tikzcd}$$

The heat of reaction ΔH_1 is given by the equation,

$$\Delta H_1 = I_{Fe^{+2}} + S_{OH} - (E_{OH} + S_{OH^-})$$

where $I_{Fe^{+2}}$ is the ionization potential of the Fe^{+2} ion in aqueous solution, S_{OH} the heat of solution of the OH radical and $(E_{OH} + S_{OH^-})$ the electron affinity of the OH radical plus the heat of solvation of the OH^- ion. The value for $I_{Fe^{+2}}$ has recently been given by Evans et al. as 94.7 kcal. (92), and for $(E_{OH} + S_{OH^-})$ as 147.6 kcal (90). The value for S_{OH} is uncertain but Evans et al. (93) consider this to be the same as the heat of solution of H_2O, namely 10.6 kcal. Inserting these values in the above equation gives $\Delta H_1 = -42.3$ kcal. Therefore, this calculation indicates that the reaction between Fe^{+2} ion and OH radical is appreciably exothermic. The large exothermicity is due largely to the high electron affinity of the OH radical plus the high heat of solvation of the OH^- ion in water. Neutralization of the OH^- ion produced in this reaction will supply an additional 13.7 kcal. It is apparent, therefore, in view of the above calculation, that the oxidation of Fe^{+2} ion by OH radicals in aqueous solution is thermodynamically probable.

An evaluation of the free energy change for this reaction may be obtained using the molar free energies of the products and reactants as given by Latimer (79). The following values are the free energies of formation at 25°C; Fe^{+2} = -20,310 cals., Fe^{+3} = -2,530 cals., OH^- = -37,585 cals., and OH_{aq} = -5,000 cals. Therefore the overall free energy change is -14,805 cals.

With this value for the free energy change and the above value for the heat of reaction, it is now possible to evaluate ΔS for this reaction.

$$\text{Since,} \quad \Delta F = \Delta H - T . \Delta S$$

$$\text{then,} \quad -\Delta S = \frac{\Delta F - \Delta H}{T}$$

Inserting the above values for ΔF and ΔH and T = 298°K, it is found that $+\Delta S = -92.3$ cals/mole/degree.

Now, the value of ΔS for this reaction is given by,

$$\Delta S_1 = S_{Fe^{+3}} + S_{OH^-} - (S_{Fe^{+2}} + S_{OH}).$$

From this equation it is possible to evaluate the term S_{OH}, i.e., the entropy of an OH radical in aqueous solution. The following values for the entropies of the aqueous ions are taken from Latimer, Pitzer and Smith (85): $S_{Fe^{+2}} = -25.9$, $S_{Fe^{+3}} = -61$, $S_{OH^-} = -2.5$. Therefore, the value of S_{OH} is found to be +54.7 cals/mole/degree. From the known value of the entropy of OH in the gas phase (86), +43.9, the entropy of solution of OH radicals in water may be obtained. This is found to be +10.6 cals/degree/mole. These values are to be considered as preliminary estimates only, since the free energy of OH in aqueous solution is not known with certainty.

The reaction between Fe^{+2} ion and the HO_2 radical is of considerable theoretical interest. There is, at the present, very little experimental evidence in support of this reaction. The heat of this reaction may be obtained from the following cycle.

$$\begin{tikzcd}
Fe^{+2}_{aq} \arrow[d, swap, "I_{Fe^{+2}}"] & + & HO_{2_{aq}} \arrow[d, swap, "S_{HO_2}"] \arrow[r, "\Delta H"] & Fe^{+3}_{aq} & + & HO^-_{2_{aq}} \\
Fe^{+3}_{aq} + e & + & HO_{2_g} \arrow[r, "E_{HO_2^-}"] & Fe^{+3}_{aq} \arrow[u] & + & HO^-_{2_g} \arrow[u, swap, "S_{HO_2^-}"]
\end{tikzcd}$$

The heat of this reaction ΔH_2 is given by the relation,

$$\Delta H_2 = I_{Fe^{+2}} + S_{HO_2} - (E_{HO_2} + S_{HO_2^-}).$$

The value for $(E_{HO_2} + S_{HO_2^-})$ has been recently evaluated by Evans et al. (90) and found to lie between 106 and 136 kcal. The uncertainty in this value is due to uncertainty in the value for the heat of the dissociation,

$$H_2O_2 \longrightarrow HO_2 + H; \qquad \Delta H = +100 \text{ kcal.}$$
$$\Delta H = +70 \text{ kcal.}$$

There is, however, evidence from the shift in the absorption maxima of the $Fe(OH)^{+2}$ and $Fe(HO_2)^{+2}$ complexes which suggests that ΔH is closer to 100 kcal (93). This suggests that the value of $(E_{HO_2} + S_{HO_2^-})$ lies closer to 136 kcal. The value for the heat of solution of the HO_2 radical in water is taken to be 12.3 kcal., i.e., the same as the heat of solution of H_2O_2 in water (93). From the work of Evans (92), the ionization potential of the Fe^{+2} ion in aqueous solution is taken to be 94.7 kcal. Insertion of these values in the above equation gives the following values for the heat of this reaction, with $(E_{HO_2} + S_{HO_2^-}) = 136$ kcal; $\Delta H_2 = -29$ kcal.

$(E_{HO_2} + S_{HO_2^-}) = 106$ kcal; $\Delta H_2 = -1$ kcal.

If, as has been indicated above, the electron affinity of the HO_2 radical plus the heat of solvation of the HO_2^- ion is closer to 136 kcal than to 106 kcal, then the heat of the reaction is found to be appreciably exothermic. In acid medium, neutralization of the HO_2^- ion would supply an additional 8.2 kcal.

The free energy change for the oxidation of Fe^{+2} ion by HO_2 radical may be evaluated using the following data for the free energies of the ions and radical in aqueous solution given by Latimer (79): $Fe^{+2} = -20,310$ cals, $Fe^{+3} = -2,530$ cals, $HO_2^- = -15,610$ cals, $HO_2 = +3,000$ cals. Consequently, the free energy change for reaction (2) is found to be -830 cals. This value plus the heat of reaction evaluated above permits the calculation of ΔS for this reaction from the relation,

$$-\Delta S = \frac{\Delta F - \Delta H}{T}$$

which gives a value of $\Delta S = -94.5$ cals/mole/degree.

The reaction between Fe^{+2} ion and H_2O_2 has been intensively studied. The reaction was originally proposed by Haber and Weiss (77) to account for the chain decomposition of H_2O_2 in the presence of Fe^{+2} ion. Recently, experimental evidence has been given by Baxendale, Evans and Park (65) which confirms that OH radicals are produced by the reaction between Fe^{+2} ion and H_2O_2. The heat of this reaction can be readily obtained from the following reactions,

$$2Fe^{+2} + H_2O_2 \longrightarrow 2Fe^{+3} + 2OH^-; \qquad \Delta H = -38 \text{ kcal.}$$

$$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^-; \qquad \Delta H = -42.3 \text{ kcal.}$$

Subtraction of these equations gives,

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH + OH^-; \qquad \Delta H_3 = +4.3 \text{ kcal.}$$

Alternatively, the heat of this reaction may be obtained from a cycle which leads to the following equation,

$$\Delta H_3 = I_{Fe^{+2}} + S_{H_2O_2} + D_{HO-OH} - (E_{OH} + S_{OH^-}) - S_{OH}$$

Insertion of the above values for $I_{Fe^{+2}}$, $S_{H_2O_2}$, $(E_{OH} + S_{OH^-})$, S_{OH} and taking D_{HO-OH} to be 55.6 kcal (92), the heat of this reaction is calculated to be +4.4 kcal. It is apparent, therefore, that this reaction is slightly endothermic. In acid medium neutralization of the OH^- ion would supply an additional 13.7 kcal. It has in fact been stated that this reaction attains maximum efficiency at pH = 1. The work of Haber and Weiss has indicated that the specific rate for this reaction is independent of pH from 0.1 N to 10^{-3} N.

A consideration of the energetics of reactions (1), (2) and (3) indicates that reaction (1) is more exothermic than reaction (2) which in turn is more exothermic than reaction (3). Therefore, the relative reactivities might be expected to be in the order (1) > (2) > (3). The much greater exothermicity of reaction (1) compared with reaction (2) is attributed almost completely to the high electron affinity of the OH radical plus the high heat of solvation of the OH^- ion. This suggests, therefore, that the OH radical is a more powerful oxidizing agent (electron acceptor) than is the HO_2 radical in aqueous solution. The energetics of reaction (2) are uncertain because of the uncertainty in the value of $(E_{HO_2} + S_{HO_2^-})$, consequently, an accurate comparison of the heat of this reaction with that of reaction (3) is not possible. The calculations do, however, indicate that reaction (2) is more exothermic than (3), the exact amount being dependent on the value of $(E_{HO_2} + S_{HO_2^-})$ that is chosen.

From the above calculations, reactions (1) and (2) are likely to be considerably more efficient than is reaction (3). These calculations may be given as further evidence that the fall off in yield below 10^{-4} M initial Fe^{+2} ion concentration in aerated solution might be due to inefficiency in the Fe^{+2}-H_2O_2 reaction.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. A kinetic study has been made of the γ-ray induced oxidation of ferrous sulfate in dilute aqueous solution, airfree and aerated.

2. The results obtained in both airfree and aerated solutions indicate that this reaction is a typical example of indirect action. Accordingly, it has been found advantageous to interpret the results in terms of the current free radical theory.

3. Airfree Solution

(a) A high vacuum technique has been developed for the preparation of airfree aqueous solutions.

(b) The initial oxidation yield, 5.1 ± 0.2 Fe^{+2} ions oxidized per 100 ev absorbed in the solution, has been found to be independent of the initial Fe^{+2} ion concentration from 10^{-3} M to 10^{-4} M. This effect has been attributed to complete removal of OH radicals by the Fe^{+2} ions.

(c) Throughout the region of concentration independence, the initial oxidation yield has been found to be proportional only to the total energy absorbed; i.e., zero order kinetics with respect to the Fe^{+2} ion concentration.

(d) Hydrogen gas is formed in an amount equivalent to the Fe^{+2} ions oxidized. Therefore, the fate of the H atoms appears to be recombination to form hydrogen gas.

(e) The addition of an excess of Fe^{+3} ions to the Fe^{+2} ion solution, prior to irradiation, had no effect on the initial oxidation yield. The decrease in yield above approximately 50% oxidation may be due to competition between molecular hydrogen and Fe^{+2} ions for OH radicals.

(f) A small positive temperature coefficient has been observed, the interpretation of which is obscure.

(g) Below an initial Fe^{+2} ion concentration of 10^{-4} M, the initial oxidation yield decreased. This may be due to (i) recombination of OH radicals in pairs, (ii) inefficiency in the reaction between Fe^{+2} ions and hydrogen peroxide. A satisfactory interpretation of this effect has not been possible with the present data. An investigation of the hydrogen gas yield below a Fe^{+2} ion concentration of 10^{-4} M would be of considerable interest.

(h) The initial oxidation yield has been found to be independent of the acid concentration from 0.8 N to 0.1 N. However, below 0.1 N the initial oxidation yield decreased rapidly with the acid concentration. The origin of this effect is not certain. Three possible explanations are considered.

(i) Airfree solutions of Fe^{+3} ion are not reduced in the presence of 0.8 N sulfuric acid. However, below an acid concentration of 0.1 N, it was observed that Fe^{+3} ions were reduced.

4. <u>Aerated Solution</u>

(a) The initial oxidation yield, 20.2 ± 0.4 Fe^{+2} ions oxidized per 100 ev absorbed in the solution, has been found to be independent of the initial Fe^{+2} ion concentration from 10^{-2} M to 10^{-4} M. This result implies that all the oxidants produced in the solution are removed by reaction with Fe^{+2} ions.

(b) The initial oxidation yield in aerated solution is approximately four times the initial oxidation yield in airfree solution. This has been attributed to the contribution of the HO_2 radical to the overall oxidation.

(c) In the region of concentration independence, the initial yield has been found to be a function only of the total energy absorbed in the solution, independent of the intensity to 100% oxidation.

(d) The addition of a large excess of Fe^{+3} ion to the Fe^{+2} ion solution, prior to irradiation, had no measurable effect on the initial oxidation yield. However, the oxidation is no longer a linear function of the energy absorbed to complete oxidation; instead, the yield decreases and tends toward an equilibrium state (compare airfree). This effect suggests that a back reaction eventually sets in.

(e) A small positive temperature coefficient has been observed, the interpretation of which is obscure.

(f) Below an initial Fe^{+2} ion concentration of 10^{-4} M, the initial oxidation yield gradually decreased (compare airfree). At these low concentrations, it has been observed that the oxidation is a linear function of the energy absorbed to approximately 70% oxidation and then appears to approach 100% oxidation exponentially.

(g) Below 10^{-4} M Fe^{+2} ion, the initial oxidation yield is inversely proportional to the intensity of the irradiation. Also, it was observed that heating the solution prior to analysis raised the initial yield to that for Fe^{+2} ion concentrations above 10^{-4} M. This effect strongly suggests the accumulation of an oxidant (probably hydrogen peroxide) in the solution.

(h) The decrease in the initial oxidation yield below a Fe^{+2} ion concentration of 10^{-4} M appears to be due to inefficiency in the reaction between Fe^{+2} ion and hydrogen peroxide.

(i) The initial oxidation yield has been found to be independent of the acid concentration from 0.8 N to 0.1 N (compare airfree). Below 0.1 N acid concentration the initial yield gradually decreased.

(j) The acid concentration has been found to have no effect on the decrease in the initial oxidation yield which sets in at a Fe^{+2} ion concentration of 10^{-4} M.

(k) Aerated solutions of Fe^{+3} ion are not reduced in the presence of 0.8 N sulfuric acid. However, below an acid concentration of 0.1 N, it was observed that Fe^{+3} ions were reduced.

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