SOME PHOTOCHEMICAL PROPERTIES OF FERRIC IRON SOLUTIONS.

R. Clark McGregor.

January 1962.

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Ann Arbor, MI 48106 – 1346

A SUMMARY OF

A THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the

requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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On irradiation, the film-covered foil shows, in a ferric chloride solution, a positive potential rise with respect to a saturated calomel electrode. It is postulated that the rise is due to the formation, by the action of light, of tetravalent iron (complex) in the film material.

In the dark there is a characteristic potential developed for various pH's in acid and alkali. On irradiation in these solutions, a rise in potential is obtained below pH 3.5 and a fall in potential is obtained above this pH value. It seems probable that the film is responding to hydroxyl radicals in a fashion similar to that in which a glass electrode responds to hydrogen ions. The film is also responsive to perhydroxyl free radicals.

Experimental evidence is given to show that the measurement of the potential difference between a platinum wire and a glass electrode presents a method of obtaining a continuous record of the changes taking place in a ferric chloride solution during irradiation. The potential is reproducible, and the electrodes themselves introduce no impurities into the system. Any drastic pH change, however, would seriously affect the potential, and this effect would require to be considered in an interpretation of the results.

There is a likeliehood that a photo-synthetic reaction with carbon dioxide may be catalysed by dilute colloidal solutions of ferric chloride. Unfortunately, however, the product (in this case oxalic acid is postulated) decomposes prior to its being isolated. There is perhaps a likeliehood that at very much lower carbon dioxide concentrations than those used, formic acid may be formed, but due to the small yield which would be obtained, and to its complexing effect with ferric iron, it is probable that a radio-labelling technique would be required before any fixation could be definitely proved.

Experiments on the addition of thallous salts as substrates to ferric chloride solutions, showed that in the systems under examination, there was a reversal of the normal iron/thallium reaction reported in the literature, i.e. in this work the thallous salt is oxidised to thallic.

This reversal would appear to be due firstly to the action of light on the system, probably causing the formation of iron(IV) on the surface of the colloidal ferric hydroxide particles, acting as an intermediate in the reaction, and secondly to the formation of strong chlorothallic complexes, retaining the thallium in its trivalent state after its photochemical formation in the system.

Work with the addition of silica gel and hydrogen peroxide to the ferric chloride solutions showed that the reaction of ferric chloride solutions is of a microheterogeneous nature, the surface of the colloidal ferric hydroxide particles being catalytically active. Conditions are established for obtaining the optimum particle size. The particle size in solutions aged 24 hours lies between 0.1 and 0.4 microns.

In ferric chloride solutions, hydrogen peroxide decomposes in a sequence of first order steps. The addition of cupric ion considerably retards the rate of decomposition of the peroxide.

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ACKNOWLEDGMENTS.

The author wishes to express his most sincere thanks to Dr. William Good for his keen interest and valuable guidance throughout this investigation and to acknowledge with gratitude the receipt of a Research Studentship from the Department of Scientific and Industrial Research.

SUMMARY AND GENERAL CONCLUSIONS.

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GENERAL INTRODUCTION.

INTRODUCTION.

Free radicals.

The vast amount of work that has been done on reaction kinetics has shown that many thermal and most photochemical reactions proceed to some extent by free radical mechanisms.

Free radicals enter into reactions with a low heat of activation and appear in low stationary concentration in pseudo equilibrium. They have a short life, due, not to instability, but rather to their high reactivity, which results in their rapid reaction with themselves or other substances present.

Free radicals which are relevant in the present work are considered below.

(a) The $\overset{\bullet}{HO_2}$ radical.

The existence of this radical was first postulated by Taylor[1], and Haber[2] first suggested that it might be invloved in the reaction between hydrogen and oxygen. The photochemical formation of hydrogen peroxide from hydrogen and oxygen was claimed by Bates and Salley[3] to invlove HO_2 radicals. An unstable product for this reaction, having an atomic ratio of one of hydrogen to two of oxygen, was isolated at low temperatures and pressures by Geib and Harteck[4]. Bodenstein and Schenk[5] attributed the inhibition by molecular oxygen of the photochemical reaction between hydrogen and chlorine to the production of these radicals. The evidence for the existence of the HO_2 radical in the gas phase has been reviewed by Minkoff[6], whilst a review of thermochemical data has been given by Gray[7].

(b) The HCO_2 radical.

This radical is an electrochemical analogue of the perhydroxyl free radical HO_2 :-

$$O_2 \xrightarrow{e^-} \xrightarrow{H^+} HO_2 \xrightarrow{e^-} \xrightarrow{H^+} H_2O_2$$

$$CO_2 \xrightarrow{e^-} \xrightarrow{H^+} HCO_2 \xrightarrow{e^-} \xrightarrow{H^+} HCOOH$$

(Kolthoff and Jordan[8]).

HCO_2 as well as HO_2 has a "symmetrical-generic" relationship (via one-electron, one-proton transfer sequences) to its parent molecule on the one hand, and to its subsequent reduction product on the other. Jordan and Smith[9] postulate its existence as an intermediate in the electroreduction of carbon dioxide at the dropping mercury electrode. Since electrode reactions represent plausible models of chemical oxidation-reduction processes[10], they maintain that HCO_2 may serve as a key intermediate in photosynthesis and in biological combustion processes, in a similar fashion to that played by HO_2 in the Haber-weiss chain sequence[11].

(c) <u>The OH radical</u>.

The hydroxyl radical, OH, was postulated by Bonhoeffer and Haber[12], Farkas, Goldfinger and Haber[13], and Haber[14] in the reaction between hydrogen and oxygen. Its occurrence was assumed in the decomposition of water vapour by Bonhoeffer and Reichardt[15]. The absorption spectrum of OH radicals was further investigated by Oldenberg and Reike[16], whilst they were shown to have quite long lives by Oldenberg[17] who used a spectrophotometric method of determining the rate of disappearance in discharge tubes.

A method of detection of free radicals developed by Evans et al[18,19], consisting of the initiation of polymerisation by the free radical, has been applied to the case of the hydroxyl radical.

Dainton[20] has demonstrated the production of OH free radicals by the short wave irradiation of water, using -rays on aqueous solutions of acrylonitrile, resulting in the initiation of chain polymerisation.

(d) The O_2^- radical-ion.

The O_2^- ion is the anion of MO_2. Potassium superoxide, which was originally given the structure M_2O_4, is paramagnetic and the X-ray study of its crystal structure by Helms and Klemm[21] revealed that the correct formula was MO_2 (M = potassium, rubidium or caesium). This was confirmed by Kassatochin[22], who with Kotov[23] had previously suggested the structure MO_2. In aqueous solution the HO_2 radical is dissociated into H^+ and O_2^- ions.

The photo-oxidation of water.

The photo-oxidation of water by ceric ions was studied by Weiss and Porret[24] who assumed the formation of an excited ceric ion, and oxygen formation would come from:-

$$Ce^{4+}H_2O \xrightarrow{h\nu} (Ce^{4+}.H_2O) \longrightarrow Ce^{3+} + OH + H^+$$

$$2OH \longrightarrow H_2O + \tfrac{1}{2}O_2$$

This photochemical reaction was carefully reinvestigated by Heidt and Smith[25] and they attributed the photochemical activity to ceric dimers. Evans and Uri[26], finding no evidence of dimerisation, postulated the ion-pair $Ce^{4+}OH^-$ as the photo-active species and were able to account quantitatively for Heidt and Smith's results. Weiss, however, stated that it cannot be ruled out that ceric ions (and other ions of a sufficiently high oxidation potential) could react directly with OH radicals according to :-

$$Ce^{4+} + OH \dashrightarrow Ce^{3+} + O + H^+$$

<u>or</u> $Ce^{4+}OH^- + \dot{O}H \dashrightarrow Ce^{3+} + H_2O + O$

i.e. the oxygen formation may not go via the intermediate formation of hydrogen peroxide.

The corresponding reaction with ferric ions was investigated by Sten and Weiss[27]. Using ferric perchlorate solutions they were able to conclude that in this case the quantum yield was certainly less than 0.01 as their apparatus was not sensitive enough to measure smaller yields.

By analogy to the ceric system, Uri[28] considers that in the photo-oxidation of water by ferric ion, the two competing reactions would be :-

$$Fe^{2+} + OH \xrightarrow{k_o} Fe^{3+} + OH^-$$

$$Fe^{3+}OH^- + OH \xrightarrow{k_1} Fe^{2+} + H_2O_2$$

In view of the considerably lower ionisation potential of ferrous ion in aqueous solution, k_0/k_1 will be much larger than in the ceric-cerous system. Furthermore, any hydrogen peroxide formed will partially re-oxidise the ferrous ion. Uri is therefore of the opinion that extremely high light intensities and also large $Fe^{3+}OH^-$ concentrations would be required to obtain measurable oxygen yields.

Dain and Kachan[29], however, have measured oxygen evolution from irradiated solutions of ferric perchlorate, quantum yields of the order of 10^{-3} being found. They attributed the photo-activity to the hydrated ferric ion $Fe^{3+}.H_2O$. In the course of investigations on polymerisation by Evans et al[30,31], a small amount of photo-reduction of ferric to ferrous ion was found in the absence of added substrate. At first it was suggested by Evans and Uri[30] that this indicated photo-oxidation of the water to oxygen :-

$$Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+} + OH$$

$$HO + OH \longrightarrow H_2O + \tfrac{1}{2}O_2$$

However, these workers now attribute this ferrous ion formation to oxidisable organic impurities in the distilled water, presumably because no oxygen was found.

More recently[32], Purdon has shown that in dilute ferric chloride solutions, water is photo-oxidised to oxygen, the ferric ion at the same time being reduced to ferrous. The photo-activity is attributed to the dimer $Fe_2(OH)_2{}^{4+}$ and possibly also to the species $Fe^{3+}OH^-$. The gas evolved was identified as pure oxygen by (a) the phosphor method of Kautsky and Hirsch, and (b) sparking with hydrogen, resulting in a 2:1 combination. The amount of oxygen was found to accord with the stoicheometry of the equation :-

$$Fe^{3+} + \tfrac{1}{2}H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + \tfrac{1}{4}O_2$$

The quantum yield with respect to ferrous ion was 0.026.

Milloy[33] provided further evidence to show that in solution ferric iron is photochemically reduced to ferrous, while water is oxidised to oxygen in accordance with the above equation. The oxygen was estimated quantitatively by two methods :-

(a) by employing the sensitive Hersch (galvanic) cell, the oxygen being first displaced from the reaction solution to the gas phase by nitrogen. (The potential difference across this cell is proportional to the concentration of oxygen in the gas surrounding a silver electrode).

(b) in the liquid phase polarographically by employing a dropping mercury electrode. The photo-reduced oxygen was identified by its double wave polarogram.

The following reaction scheme was proposed to account for the photo-oxidation :-

Primary reaction :-

(a) $FeOH^{2+} \xrightarrow{h\nu} Fe^{2+} + OH$

(b) $Fe(OH)_2^{+} \xrightarrow{h\nu} Fe^{2+} + OH + OH^-$

followed by the back reaction :-

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

then formation of hydrogen peroxide by one or more of the following steps :-

$$OH + OH \longrightarrow H_2O_2$$

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

$$Fe(OH)_2^{+} + OH \longrightarrow Fe^{2+} + OH^- + H_2O_2$$

and decomposition of the hydrogen peroxide by iron catalysis :-

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

The quantum yield for ferrous ion formation was found to be $\phi_{max} = 0.05$.

The effect of light on hydrolysis.

ferric chloride, being the salt of a strong acid and a weak base, immediately hydrolyses when dissolved in water, to give an acid solution. This primary hydrolysis is followed by a much slowere hydrolysis which may take a variable time for completion, depending on such conditions as temperature and concentration. During this secondary hydrolysis there is a decrease in pH, accompanied by the appearance of a reddish-brown colour of colloidal ferric hydroxide which may ultimately precipitate out.

It was Lamb and Jacques[34] who first attempted a quantitative correlation of their experimental data with a proposed mechanism. The explanation suggested was that as soon as the ferric salt dissolves, a rapid reversible hydrolysis ensues giving rise to a number of hydrolysis products, but in particular to a dilute but supersaturated solution of ferric hydroxide :-

$$Fe^{3+} \overset{H_2O}{\rightleftharpoons} \underset{\substack{+\\ H^+}}{FeOH^{2+}} \overset{H_2O}{\rightleftharpoons} \underset{\substack{+\\ H^+}}{Fe(OH)_2^{+}} \overset{H_2O}{\rightleftharpoons} \underset{\substack{+\\ H^+\\ \text{dissolved}}}{Fe(OH)_3} \rightleftharpoons \underset{\text{colloidal}}{Fe(OH)_3}$$

The coagulation to form colloidal ferric hydroxide is the controlling, relatively slow step, in this reaction, the rate of hydrolysis being proportional to the degree of supersaturation in the solution of the undissociated ferric hydroxide.

At the beginning of this century, Moore[35] found that light had no effect on the initiation of the hydrolysis of ferric iron solutions. However, Bhatnager[36], Zocher and Heller[37] and Heller[38], suggested that although light is not active in the initiation of the hydrolysis, it does accelerate the coagulation of the ferric hydroxide once formed.

Purdon[32], in the course of experiments on the photoreduction of ferric chloride, observed that a reddish brown colour formed during irradiation, whereas another portion of the same solution standing in the dark at the same temperature remained colourless for over two hours. He concluded that the effect of light was to accelerate the hydrolysis. He suggested that the accelerating action of light on the hydrolysis might be due to the reaction of ferrous ion and hydrogen peroxide, the environment of the freshly produced ferric ion being such that complete hydrolysis takes place.

Milloy[33] also observed this acceleration of hydrolysis on irradiation.

He proposed that the phenomenon was due mainly to the reaction :-

$$Fe(OH)_2^+ \xrightarrow{h\nu} Fe^{2+} + OH + OH^-$$

which is seen to produce OH^- ions which are unlikely to be removed by the back reaction of $Fe^{2+} + OH + OH^-$ since this would involve termolecular collisions. He therefore suggests that the sudden production, by irradiation, of OH^- ions by the above reaction could then lead to :-

$$Fe(OH)_2^+ + OH^- \longrightarrow Fe(OH)_3$$

The resulting increase in the concentration of dissolved ferric hydroxide would break down the supersaturation and provide the nuclei which initiate the hydrolysis.

The effect of hydrogen peroxide on the "light" and "dark" hydrolysis was also studied and it was found that the acceleration of the hydrolysis produced by light was strongly diminished. Although no adequate explanation of the effect of hydrogen peroxide on the "light" hydrolysis was found, Milloy concluded that the accelerating effect of light on the hydrolysis was not due to a reaction between hydrogen peroxide and ferrous ion.

Lamb and Jacques[39] have shown that all solutions of ferric chloride less concentrated than 0.1M are supersaturated with respect to ferric hydroxide. This was in accordance with the observation that the 1.3×10^{-3}M ferric chloride solutions employed throughout this and earlier studies were very delicately poised with regard to secondary hydrolysis (the formation of colloidal ferric hydroxide always seemed imminent from the moment of preparation of the solutions). Milloy therefore suggested that any reaction which led to the production of ferric hydroxide nuclei on which dissolved ferric hydroxide could further deposit, would accelerate the hydrolysis.

The photo-active species in 1.3×10^{-3}M ferric chloride.

In solutions of ions which readily form complexes, it is sometimes difficult to decide which species are present, and of these which, if any, are photo-active. The relative concentrations of the species are dependent on many factors, e.g. temperature, ionic strength, pH, etc.

The existence of the dimer $Fe_2(OH)_2^{4+}$ was first suggested by Hedstrom[40] following an investigation on the hydrolysis products of ferric ion by new e.m.f. methods. The dimer formation was represented by :-

$$2Fe^{3+} + 2H_2O \longrightarrow Fe_2(OH)_2^{4+} + 2H^+$$

Further evidence of dimer formation was subsequently reported by Milburn and Vosburgh[41] and Mulay and Selwood[42] from magnetic and spectrophotometric studies on ferric perchlorate solutions.

With aqueous ferric chloride solutions, the existence of ferric-chloro complexes must also be considered. Rabinowitch and Stockmeyer[43] suggested that a solution of ferric chloride could contain all the species, Fe^{3+}, $FeCl^{2+}$, $FeCl_2^{+}$, $FeCl_3$, $FeCl_4^{-}$, $FeCl_5^{2-}$ and $FeCl_6^{3-}$, and from spectrophotometric studies obtained values for the stability constants of $FeCl^{2+}$, $FeCl_2^{+}$, and $FeCl_3$. Camlen and Jordan[44] conclude that the highest chloro-complex formed is $FeCl_4^{-}$. Consideration of the data given by them indicates that under the conditions applying in the solutions of the present investigation, only the complexes $FeCl^{2+}$ and $FeCl_2^{+}$ are present in significant amount.

From a consideration of spectral curves Milloy deduced that at a pH of 3.05, the predominant species are $Fe(OH)^{2+}$ and $Fe(OH)_2^{+}$, whilst at pH 2.20, the predominant species are $FeOH^{2+}$ and Fe^{3+}. The concentration of these species over the pH range 2.20 - 3.05 is given, as is the concentration of other species present in smaller amount, viz :- $Fe(OH)_2^{4+}$, $FeCl^{2+}$ and $FeCl_2^{+}$.

The catalytic decomposition of hydrogen peroxide.

Many investigations of the homogeneous iron salt catalysed decomposition of hydrogen peroxide in dilute aqueous solution have been described. The field has been reviewed by Baxendale[45] and Weiss[46].

Kinetic experiments in dilute solution have led to the conclusion that the key reaction is of the form :-

$$Fe^{3+} + H_2O_2 \dashrightarrow Fe^{2+} + HO_2 + H^+$$

or $$Fe^{3+} + HO_2^- \dashrightarrow Fe^{2+} + HO_2$$

There are various schools of thought as to the details of the further stages of the reaction, but all models involve the radicals OH and HO_2 as intermediates, following the theory of Haber and Weiss[47]. All the models are amplifications of von Bertalan's suggestion[48] that the catalysis occurs as a result of the alternating reduction of ferric and oxidation of ferrous according to the overall reactions :-

$$2Fe^{3+} + H_2O_2 \dashrightarrow 2Fe^{2+} + 2H^+ + O_2$$

$$2Fe^{2+} + H_2O_2 \dashrightarrow 2Fe^{3+} + 2OH^-$$

The possible mode of intervention of the ferric-peroxy complex in the reaction was considered[49] according to :-

$$Fe^{3+} + HO_2^- \rightleftharpoons (FeHO_2)^{2+} \dashrightarrow Fe^{2+} + HO_2$$

In support of this scheme, no deviation from first order dependence on peroxide concentration was observed in the dilute aqueous hydrogen peroxide solutions employed.

The primary step suggested by Haber and Weiss in the ferric iron catalysis is :-

$$Fe^{3+} + HO_2^- \dashrightarrow Fe^{2+} + HO_2$$

It had been known for some time that the rate constant was proportional to the concentration of ferric iron and hydrogen peroxide and inversely proportional to the acidity, an observation which would be in agreement with the assumption that HO_2^- was the reactive entity. Subsequently a chain reaction, as in ferrous iron catalysis or a reaction with ferric iron of the HO_2 radical, i.e.

$$Fe^{3+} + HO_2 \dashrightarrow Fe^{2+} + O_2 + H^+$$

would lead to the evolution of oxygen.

Weiss suggested that the HO_2 radical is dissociated in aqueous solution into H^+ and O_2^- ion, and HO_2 should be replaced by the latter in the scheme.

Bray and Gorrin[50] suggested an alternative chain mechanism to that of Haber and Weiss which involved the formation of the tetravalent iron ferryl ion :-

$$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O$$

$$FeO^{2+} + H_2O_2 \longrightarrow Fe^{2+} + H_2O + O_2$$

This mechanism was later revised by Medalia and Kolthoff[51], but it was pointed out by Uri[52] that it was unlikely on the principle that reactions for which no simple mechanism involving only bond breaking and electron transfer can be devised are less probable. The formation of ferryl ion by a different mechanism was suggested by Barb, Baxendale, George and Gargrave[49] :-

$$Fe^{3+} + OH \longrightarrow FeO^{2+} + H^{+}$$

but they are not convinced that the experimental evidence for its occurence is conclusive.

Andersen[53] observed that with lower peroxide/ferric ion concentration ratios, deviations from first order decomposition occur and proposed a mechanism, later revised by Christiansen and Andersen[54] to explain it. Uri[28] claims that their scheme is unacceptable. However Barb et al[49] and Weiss[55] show that Andersen's results can be accounted for by assuming that the catalytic decomposition of hydrogen peroxide by ferric ion is a chain reaction produced by the small but measurable concentration of ferrous ion.

George[56] has investigated the reactions of KO_2 in water and hydrogen peroxide and found no evidence for a reaction between O_2^- and H_2O_2. It was pointed out by Dainton and Agar[57] that no conclusions can be drawn from George's observations on the likelihood of the latter reaction in the homogeneous phase in view of the alkaline environment of the KO_2 crystals.

That the Haber-Weiss mechanism holds also in the case of permolybdic and pertungstic acid has been shown by Uri[58] in a kinetic study of the catalytic decomposition of hydrogen peroxide by molybdic and tungstic acid in the presence of Cu^{2+} ions and some complexes of the latter.

Jones, Kitching, Tobe and Wynne-Jones[59] working on the ferric ion catalysed hydrogen peroxide decomposition propose a scheme in which the water molecules in the solvation shell of the ferric ion are replaced by molecules of hydrogen peroxide to give ferric-peroxy complexes of the type $Fe(H_2O)_5(H_2O_2)^{3+}$. The kinetics of the reaction are compared and are found to be consistent with the radical mechanism originally proposed by Haber and Weiss for the reaction in dilute solution.

Following on this, Haggett, Jones and Wynne-Jones[60] suggest the importance of ferric-peroxy complexes as intermediates in the reaction. Spectrophotometric evidence for the existence of complexes of the type proposed is described. Measurements of the kinetics of chromium(VI)-salt catalysis of the decomposition of hydrogen peroxide in H_2O_2/H_2O mixtures are also reported, and the results are shown to be consistent with the model proposed for iron salt catalysis. The analogy between the proposed model and an enzyme reaction is pointed out.

Bohnson and Robertson[61] found that a small addition of cupric ion caused an increase in the rate of decomposition of hydrogen peroxide far in excess of that expected from the sum of the rates for ferric and cupric ions acting independently. This enhanced rate reached a limit at which further additions of cupric ion had little effect.

This is explained on the basis that cupric ion reacts more rapidly than ferric ion with the radical HO_2, causing an increase in the rate of decomposition by reducing the amount of HO_2 available for termination by :-

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

and leading to a change over from termination by this reaction to termination by :-

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

when effectively all HO_2 reacts with either cupric ion or ferric ion. Under these conditions the rate becomes independent of cupric concentration and second order with respect to peroxide.

Electrode systems in irradiated solutions.

The photo-voltaic effect is defined[62] as the production or change of a potential difference between two electrodes separated by a suitable electrolyte or other substance when the electrodes are unsymmetrically illuminated. It is also called the "Becquerel effect" in honour of its discoverer. Similar to this effect is the "Swensson-Becquerel effect", which is the production of a photo-potential upon illumination of one electrode only.

It has also been found that the gamma irradiation of an entire electrochemical system containing an aqueous electrolyte and metal electrodes produces hydrogen and hydroxyl radicals in the bulk of the solution, and electrons, derived from Compton scattering, near the electrode surface. These species may participate in electrochemical processes and modify the appropriate electrode kinetics. Several changes in electrode behaviour have been reported in various cells irradiated with a gamma source[63-66], and irradiation with ultra-violet light has been shown to affect overpotential relations[67]. However no complete systematic study of the effects of radiation have been made. The physical state of the electrode metal, and its pre-treatment, are known to influence the kinetics of electrode reactions[68].

Feates[69] reports the effects of gamma radiation on smooth platinum electrodes in aqueous solutions. Characteristic changes in rest potential are shown to arise from competition for adsorption sites on the metal surface by radiolytically generated hydrogen and hydrogen peroxide. The potential-determining species in H_2O_2 solutions has been shown to be the HO_2 radical.

Changes in the kinetics of the evolution of hydrogen at electrodes have been studied and these changes are very sensitive to electrode pre-treatment. Large changes of Tafel slope are reported for electrodes prepared in the absence of hydrogen, in the presence of air, but much smaller changes for electrodes prepared in hydrogen. This is interpretated in terms of the differing sensitivities of the electrode surfaces to hydrogen and hydrogen peroxide.

Differential irradiation of the electrochemical cell has been studied as a possible means of direct conversion of radiation energy and an efficiency of 1.3% has been achieved.

Dainton and Collinson[70], developing a suggestion of Allen[71], proposed that irradiation of an aqueous redox solution ultimately leads to the generation of a constant redox ration, determined solely by the relative oxidising and reducing powers of the radiolytically generated radicals OH and H. They expressed this property of the irradiated water as an "equivalent redox potential" (ERP) which should be characteristic of water alone and independent of any particular redox solute employed.

The work has recently been extended by Henderson, Lovering, Haines and Casey[72] who found a very reproducible potential was ultimately obtained when a wide range of redox systems was irradiated with X-rays. They determined the pH dependence of the potential which was linear and satisfied the relation $E_{ERP} = 0.85 - 0.059pH$. They therefore concluded that this represented the true ERP. However no account was taken of the generation of free hydrogen peroxide in the later stages of irradiation, although potentials measured in redox systems are often very sensistive to H_2O_2[73].

Mendelovsky, Bakh and Zhuraskaya[74] have carried out a detailed potentiometric investigation of the X-ray oxidation of ferrous iron in nitrogen-saturated aqueous solutions. They found that the relationship between potential and radiation dose was very similar to a conventional redox titration curve and they therefore assumed the electrodes responded only to the normal redox species. At high degrees of oxidation, in the region where the so-called ERP is operative, a post irradiation effect was observed, which was attributed to the non-irradiation oxidation of the remaining ferrous iron by free hydrogen peroxide in the solution.

Feates and Knight[75] showed that these after-effects arose from a change in the concentration of radiolytically generated hydrogen which was found to be an important potentiometrically active species throughout the whole course of oxidation. The equilibrium potential ultimately obtained during the irradiation of aqueous redox systems was shown to be due to the effects of hydrogen peroxide, and not, as previously reported, to an equivalent redox potential. The equivalent redox potential was not confirmed by these workers as they did not have available a sufficiently effective and specific hydrogen peroxide scavenger which was not electrochemically active.

The present investigation.

The present work is a further investigation of some of the photochemical and associated properties of ferric iron solutions. Experiments are described on the effect of the solutions on platinum electrodes, both with regard to a photovoltaic or "Becquerel" effect on immersed electrodes and to an investigation of the redox potential and pH changes of the solution during its irradiation.

The effect of carbon dioxide on the properties of the solutions has been studied, as has also the effect of various other substrates, such as thallium salts, silica gel and phosphates.

Results are given for experiments carried out on the catalytic decomposition of hydrogen peroxide which is believed to be formed as an intermediate in the photo-oxidation of water.

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PART 1.

Photovoltaic effect, redox potentials and allied electrochemical properties during the photo-reduction of dilute ferric iron solutions.

INTRODUCTION.

This investigation of some of the electrochemical properties of the aqueous ferric chloride system falls into two parts, viz., investigation of the photovoltaic or "Becquerel" effect on immersed electrodes, and investigation of the redox potential and pH change of the solution during its irradiation.

(a) The photovoltaic effect.

Purdon[32] has shown that during the photochemical reaction of ferric chloride solutions, reduction of the ferric iron takes place in the bulk of the solution or at the interface of any inert solid phase which may be present, such as silica.

The presence therefore, of an illuminated electrode of polished platinum, providing as it does an interface, should furnish information as to the nature of the photoreaction taking place at the surface. If, for example,

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

takes place, then the electrode should become positive with respect to the solution.

The investigation however is complicated by the potential generated by a possible photovoltaic effect.

This potential may be a resultant of more than one mechanism. It is not instantaneous. The time taken to reach a steady potential depends on the system. For a light-sensitive electrolyte this potential has been found by a large number of workers listed in the review by Baur[76], to depend on the following factors :-

(a) pH of the solution.

(b) temperature of the solution.

(c) concentration of the solution.

(d) frequency of light used. (athreshold frequency exists).

A thermoelectric effect is present in some cases and the state of the surface of the electrodes has some influence on the potential.

Baur[76] obtained a small positive potential on irradiation of ferric-ferrous chloride solutions. He ascribed this as being due to the photolysis of water.

Swenson[76] rejected this, since no H_2, H_2O_2, O_3 or O_2 was detected, but in view of the work of Purdon[32] and Milloy[33] it was decided to re-open the investigation.

Audubert[77] accounts for the potentials obtained in acid-stabilised solutions of ferric and ferrous salts by adapting the Perrin-Lewis theory of radiation chemistry, to obtain the relationship :-

$$Q = Nh(\nu'_o - \nu_o)$$

where Q = heat of reaction

ν'_o, ν_o = threshold frequencies for Fe^{3+} and Fe^{2+} respectively.

The ferric potential is positive, and the ferrous negative. This view agrees well with the heat of reaction obtained from the cell :-

$$Pt, H_{2(g)} \quad acid \quad satd.\ KCl \quad Fe^{3+}, Fe^{2+} \quad Pt$$

by means of the Helmholtz equation.

Thus Audubert gives the reaction taking place as :-

$$2Fe^{3+} + H_2 + 2h\nu \rightleftharpoons 2Fe^{2+} + 2H^+ + 2h\nu$$

It was thought that possibly the use of dilute unstabilised ferric chloride systems might invalidate this interpretation and favour the photolysis theory of Baur.

(b) Redox potential and pH change.

In previous work carried out on ferric chloride solutions by Purdon and Milloy, any estimation of the ferrous iron formed was made by withdrawal of samples from the irradiated solution. Due to volume change, this withdrawal may cause unknown side effects in the system, and, in any case, can only supply an intermittent record of the quantity of ferrous iron which is being produced.

The quantity of ferrous iron may, however, be estimated from the redox potential, after determination of the constants for the system. The "Nernst" equation ststes :-

$$E = E_o + \frac{RT}{nf} \ln a_{oxid}/a_{red}$$ (using European convention)

where E_o is the standard redox potential of the system.

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + ne$$

The difficulty lies in assigning a formula to the oxidant. For example, according to Purdon, a few of the possible equilibria which may exist at the electrode are :-

$$Fe_2(OH)_2{}^{4+} + 2e^- \xrightarrow{h\nu} 2Fe^{2+} + 2OH^-$$

$$Fe(OH)^{2+} + e^- \xrightarrow{dark} Fe^{2+} + OH^-$$

$$Fe^{3+} \text{ aq.} + e^- \longrightarrow Fe^{2+} \text{ aq.}$$

The equilibrium constants for these reactions will determine the relative properties of the Standard Electrode Potentials which make up a Standard Electrode Potential for the irradiation reaction.

Another complicating factor in both the photoreduction and redox equilibria is the effect of pH. As pH decreases, the concentration and therefore absorption fractions of each species change.

The effect of the pH change on the redox equilibria can be more easily assessed if the equations are written in the form, e.g. :-

$$Fe^{2+} + H_2O \rightleftharpoons Fe(OH)^{2+} + e^- + H^+$$

So :-

$$E = E_0 + 0.058 \log\left[\frac{Fe(OH)^{++}}{Fe^{++}} - pH\right] \quad \text{(European convention)}$$

The change in H^+ ion activity of dilute ferric solutions has been extensively studies by Lamb and Jacques[39]. Their work shows that the primary hydrolysis is followed by a secondary hydrolysis which produces colloidal ferric hydroxide. (see page 9.)

The rate of this secondary hydrolysis is proportional to the degree of supersaturation of $Fe(OH)_3$ in solution. The colloidal $Fe(OH)_3$ is in heterogeneous equilibrium with the $Fe(OH)_3$ in solution, but only for very dilute solutions, does the reaction reach this equilibrium. Any alteration in temperature will cause the system to re-adjust itself, although slowly at low temperatures.

It can be seen that this hydrolysis, which leads to a decrease in pH, is of some importance in determining the photo-active species, and that the pH will have an effect on the redox potential measured. It is thus necessary to determine the pH along with the redox potential of the system during irradiation.

EXPERIMENTAL.

The construction and use of an electrometer unit.

In the measurement of potential changes taking place on an electrode as a result of illumination, it was necessary to consider avoiding destruction or modification of the changes caused by drawing too much current. To ensure that the current would be minimal, it was decided to construct an electrometer unit which would require no more than about 10^{-13} to 10^{-14} amps. in the registration of the potential.

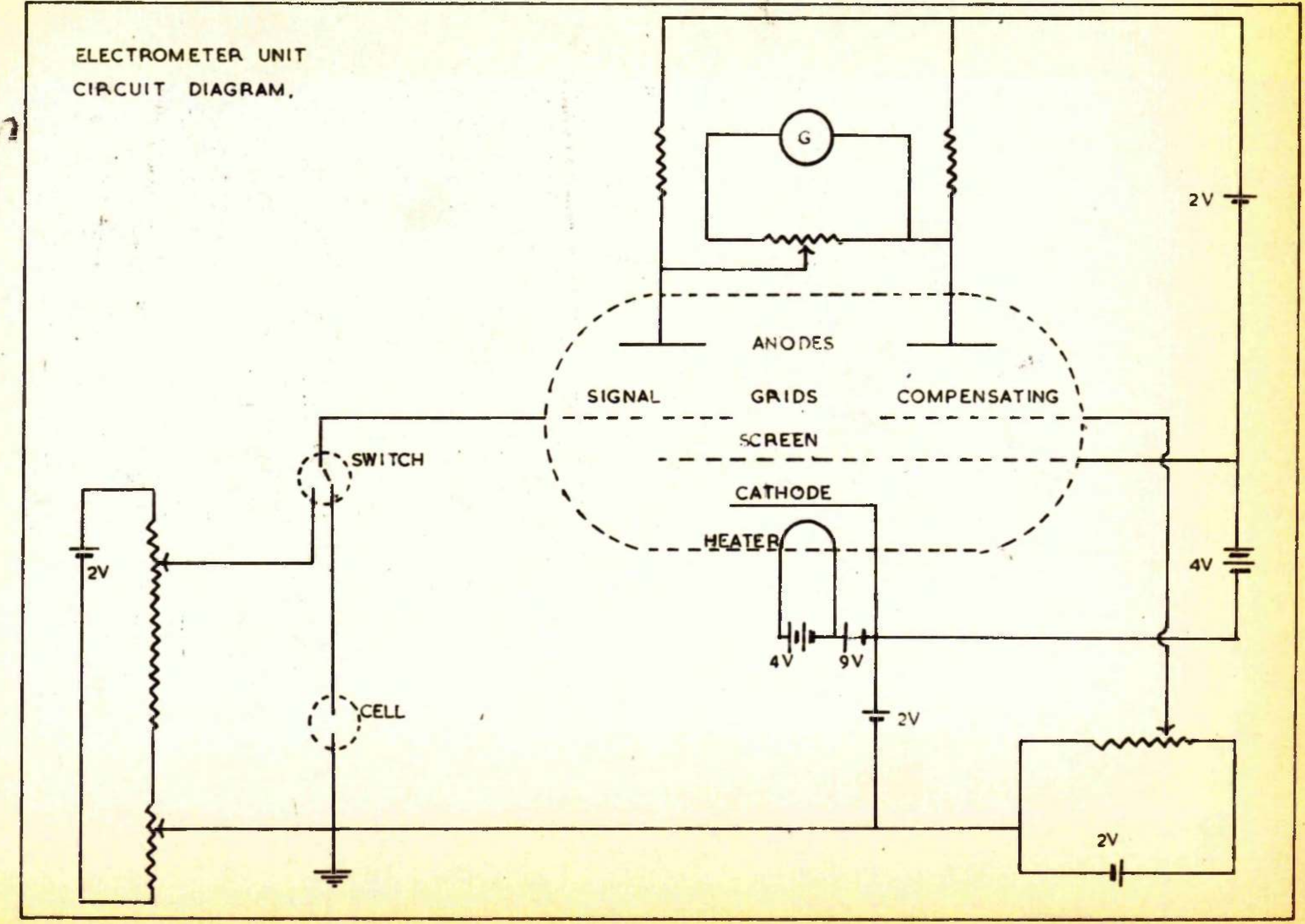
A circuit diagram for the electrometer unit is given in fig.1. Essentially the unit comprises :-

(a) the valve (an electrometer tetrode).
(b) a switch, by means of which either
(c) s standardised potentiometer input, or
(d) the unknown cell voltage, can be fed to the control grid of the valve;
(e) a circuit for the variation of compensating control grid potential;
(f) a circuit, incorporating a galvanometer, to balance the anode potentials.

(a) A Ferranti B.D.M. 10 valve was used. This is of the double tetrode type, having in addition to the three normal electrodes, a screen. The latter is maintained at a positive potential of four volts relative to the cathode, thereby reducing cation emission. The valve possesses two anodes and two grids, and operates on a comparative basis. The internal arrangement of the electrodes is shown in fig.1. To reduce leakage, the grids are constructed on an insulated mounting, and the external connections leave the valve through the top, i.e. in the opposite direction from the other electrodes. Further, the valve is fitted with internal and external guard rings, maintained at a potential equal to that of the compensating control grid. The silicone-coated glass envelope must be kept dry and clean. The valve was mounted, together with the switch, in a closed, rectangular, aluminium box. This was found to provide adequate electrical and magnetic screening.

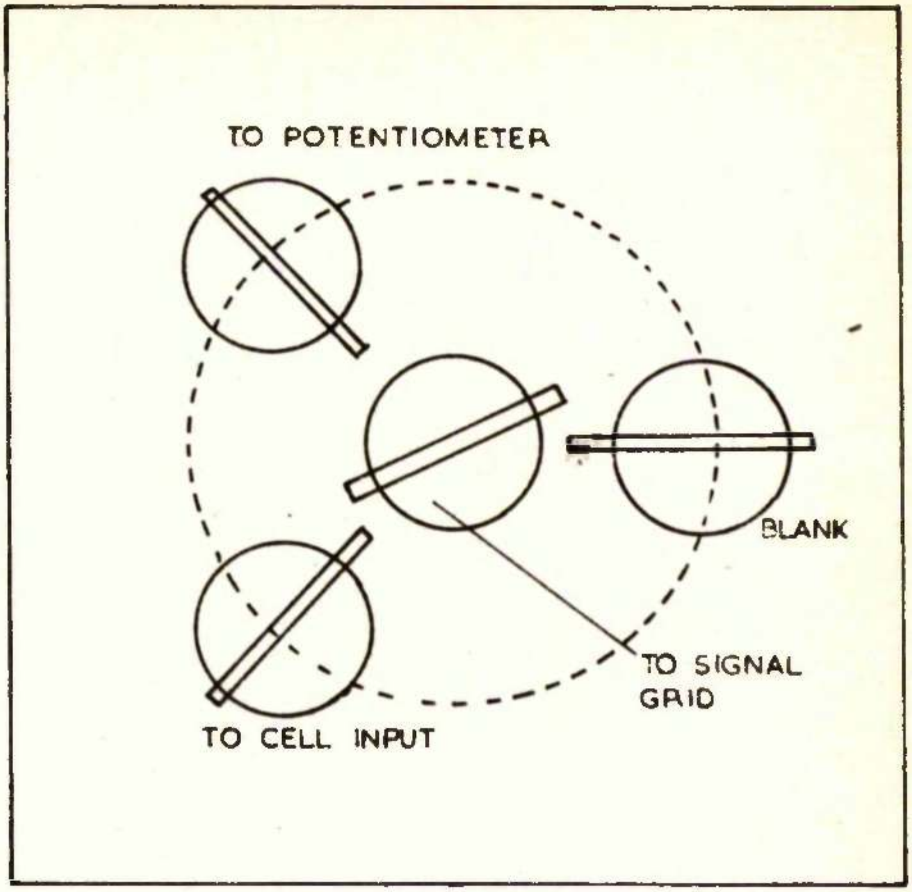
(b) A diagram of the three-way switch arrangement is given in fig.2. The circuit connections were placed at the lowere ends of four pillars. Three of theses were fixed, two being wired to the potentiometer and the cell respectively, and the other blanked. The latter was provided in case of further modification. The remaining pillar, centrally placed, could be rotated to contact any of the

FIGURE I.



ELECTROMETER UNIT
CIRCUIT DIAGRAM.

FIGURE 2.



THREE-WAY SWITCH LAYOUT

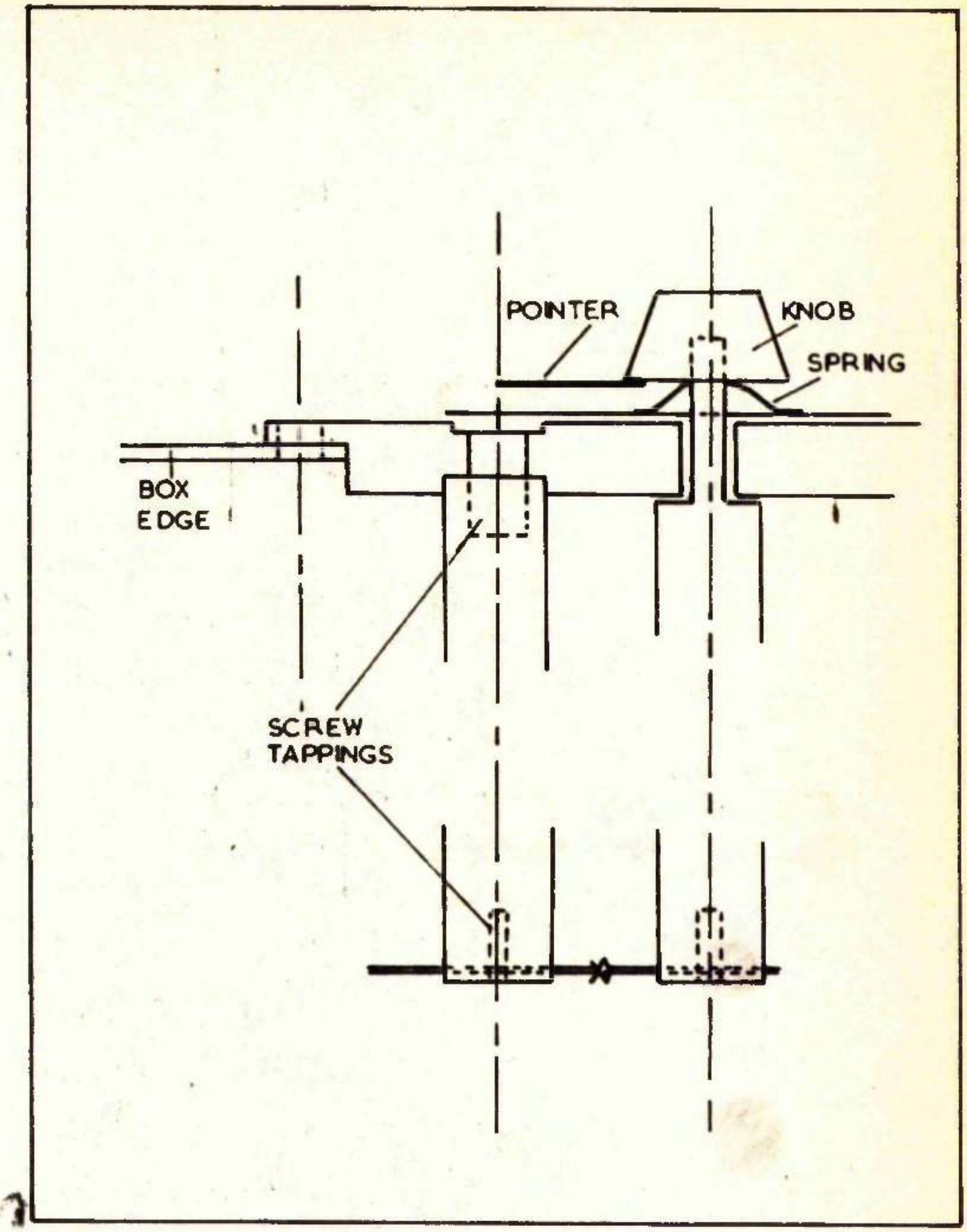
fixed connections, and was wired to the signal control grid, i.e. the latter could be linked to either the potentiometer or the cell as desired.

The pillars were ½" in diameter and 2½" in length, and were of polystyrene. The three fixed pillars were secured to the circular bakelite top-piece by ⅜" screws. The central pillar projected through the top-piece, was attached to a knob, and held rigid by a small piece of spring steel. To indicate the position of this pillar, the knob was fitted with a pointer. Bolts secured the unit to the mounting box. The circuit connections at the bottom of the fixed pillars consisted of 1" flat brass plates secured by clips. To the central pillar was fixed a small spring clip. Connection was established by the brass plate entering between the lips of the clip. These constructional details are sketched in fig.3.

Polystyrene provides a high degree of insulation in the absence of surface films. The latter was ensured by washing in ethanol before mounting.

(c) As a source of accurately known potential, a Tinsley potentiometer, slightly modified, was used. Standardisation was effected in the normal manner, using a Weston cell.

FIGURE 3.



CONSTRUCTIONAL DETAILS OF THREE-WAY SWITCH.

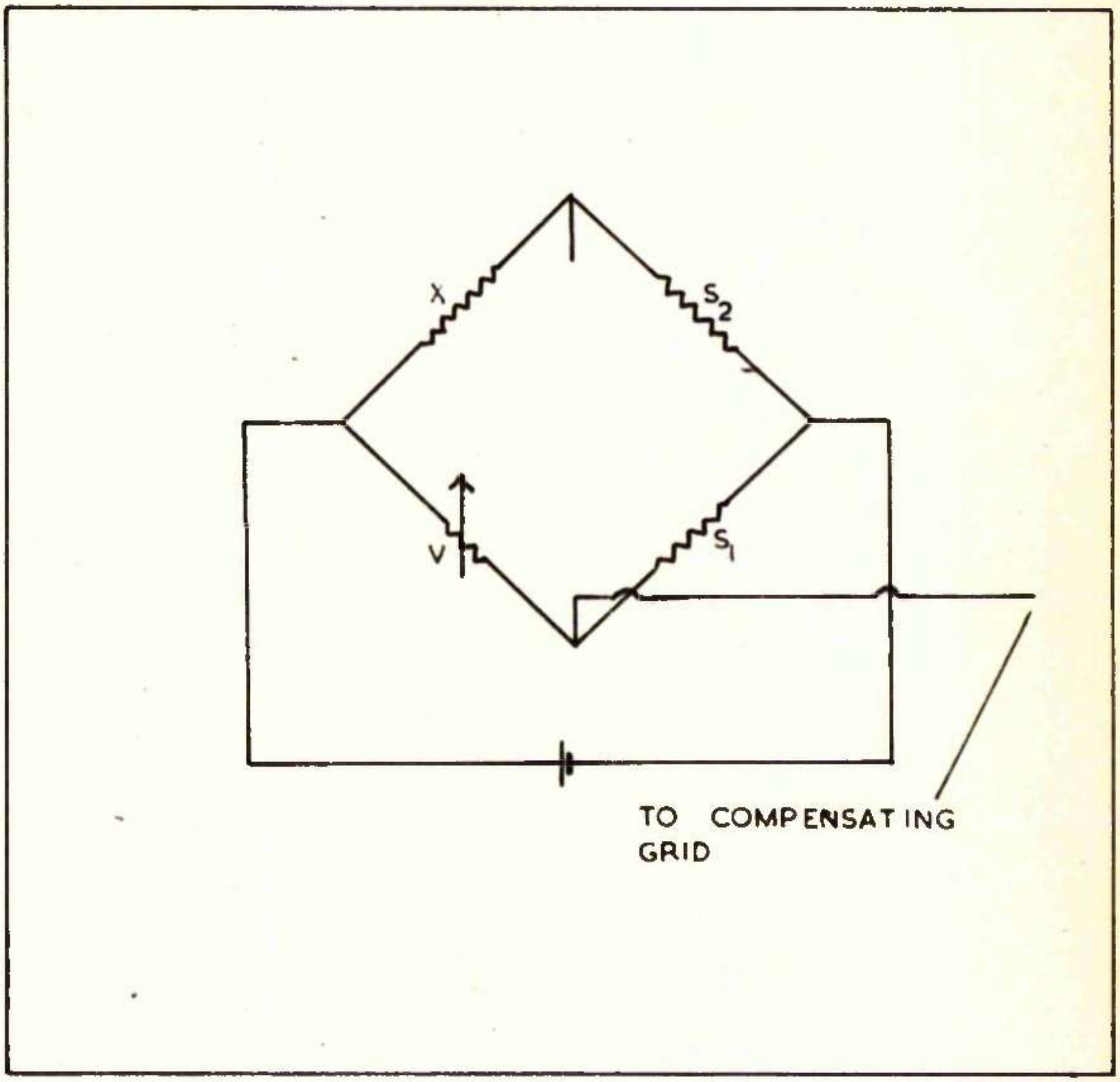
(e) To vary the potential of the compensating control grid, the modified Wheatstone bridge circuit shown in fig.4 was used. This replaced a simple wire wound resistance, which gave a noticeably discontinuous voltage variation. In the present circuit, the grid potential altered with the resistance V. A resistance of 10^3 ohms (S_1) was permanently in the circuit, preventing any serious drain on the battery. V was variable in steps of one ohm, which for this system, was equivalent to virtual continuity. The internal and external guard rings were wired to this point.

(f) The operation of the unit, described below, depended on balancing the anode potentials. This was achieved simply by a standard galvanometer-shunt circuit, wired between the anodes.

As a source of E.M.F., two-volt accumulators were used throughout, except for the nine-volt heater-cathode voltage, where a dry grid bias battery was used. To ensure stability, fully charged accumulators were run down by roughly 30% of their capacity before use.

The circuit was switched on for about one hour before use, to allow the valve and ancillary equipment to reach stable working conditions. The switch was set to feed

FIGURE 4.



COMPENSATING GRID CIRCUIT

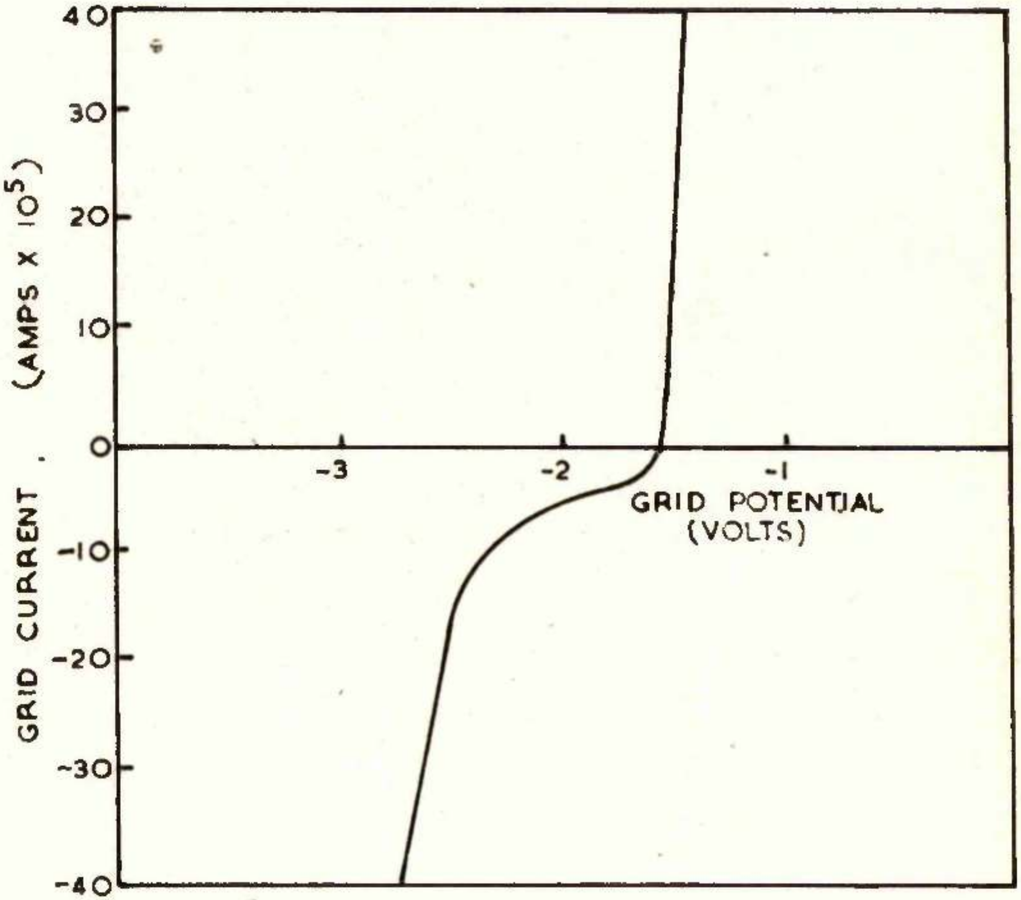
the cell voltage to the signal grid. The compensating control grid voltage was then adjusted until zero deflection was observed on the anode circuit galvanometer, i.e. both anodes had the same potential.

On reversal of the switch, the potentiometer input was fed to the signal grid, and adjusted until zero deflection was obtained once more. The compensating grid having remained at constant potential throughout, it follows that the cell and potentiometer inputs must be equal in magnitude and could be read directly from the latter instrument. In essence, the instrument operates by quantitative comparison of the unknown voltage and a measured input.

The stability of the unit under normal conditions was very satisfactory, galvanometer drift being apparently non-existent. Intermittent pulse-like disturbances were observed, but interfered little with ease of measurement, and were attributed to electrical effects arising from other appliances in the laboratory. Sensitivity was high, and using zero deflection method of operation described, with minimum shunt resistance in the galvanometer circuit, an accuracy of ± 0.1m.v. was readily obtained. Some preliminary tests were carried out with a very high resistance in the signal grid input circuit, and a tendency to instability noted. This could probably have been eleiminated by the use of screened cable in the signal grid circuit.

The circuit was originally designed to measure voltages of 500 m.v. maximum, but later modifications of the irradiation cell, using the valve voltmeter, required that higher input potentials of about 800 m.v. be measured. The effect of this si evident on reference to the signal grid characteristic curve shown in fig.5[78]. Deviations of grid potential from the zero input value of -2 v. greater than ± 500 m.v. will result in an appreciable current, defeating the purpose for which the unit was designed. A simple and effective method of surmounting this difficulty was to introduce a standard cell, in series with and in opposition to, the cell voltage being measured. The use of a Weston standard cell, of constant potential 1.01856 v, permitted the measurement of voltages within the approximate limits 500 - 1500 m.v. without taking a damaging current from either of the cells. Alternatively, a standard potentiometer could be used. This had the advantage of greater flexibility, but was clumsier and required frequent standardisation.

FIGURE 5.



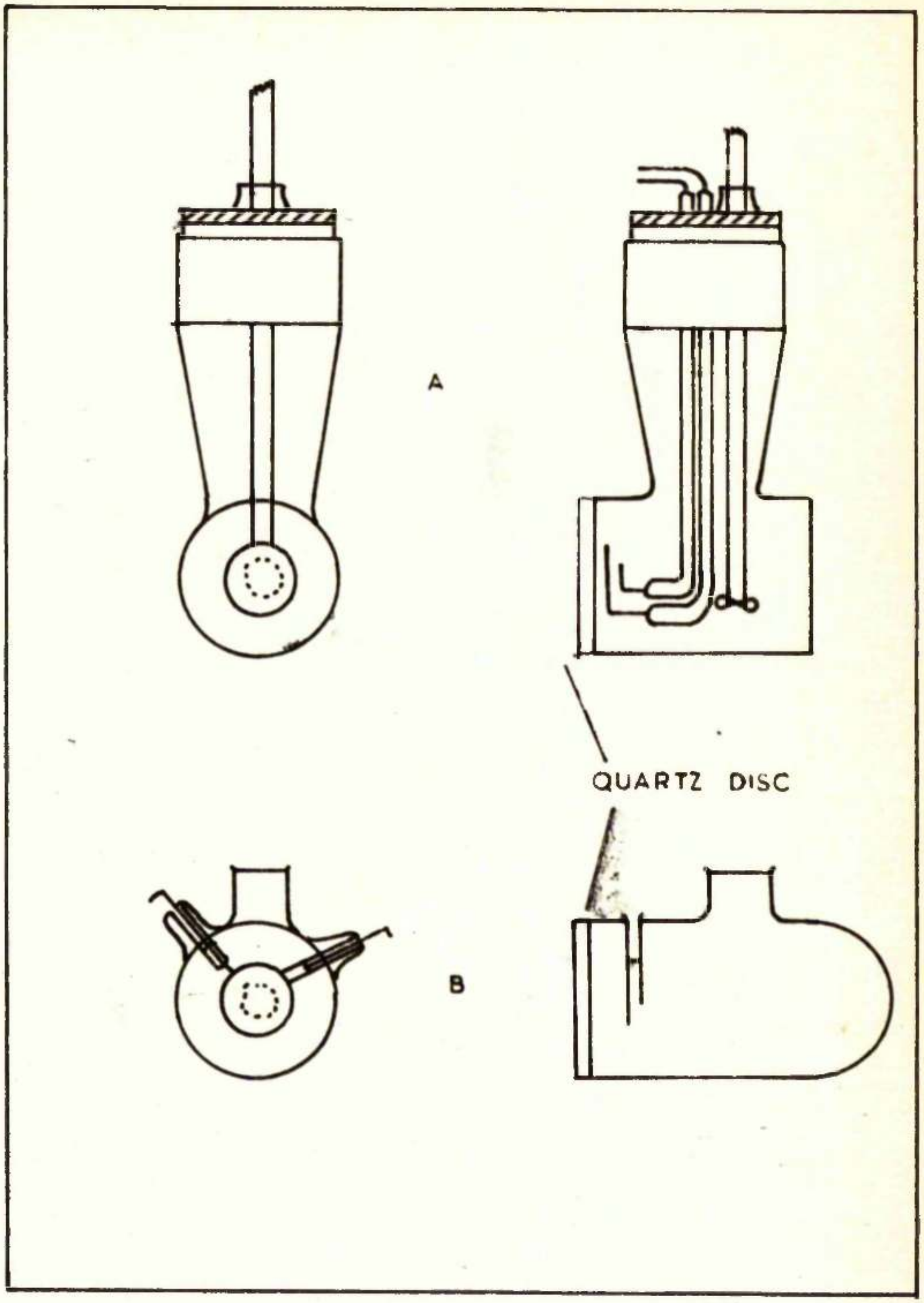
SIGNAL GRID CHARACTERISTIC CURVE.

Photo-voltaic irradiation apparatus.

Two cells, as illustrated in fig.6 were used in early work on the investigation. Neither was perfectly satisfactory, the first because of the possible movement of the electrode, the second because of the necessity to use "Araldite" cement to fix the quartz disc in position. This increased the risk of organic impurities in the solution. The cells were continuously sprayed during irradiation to maintain their contents at 20°C.

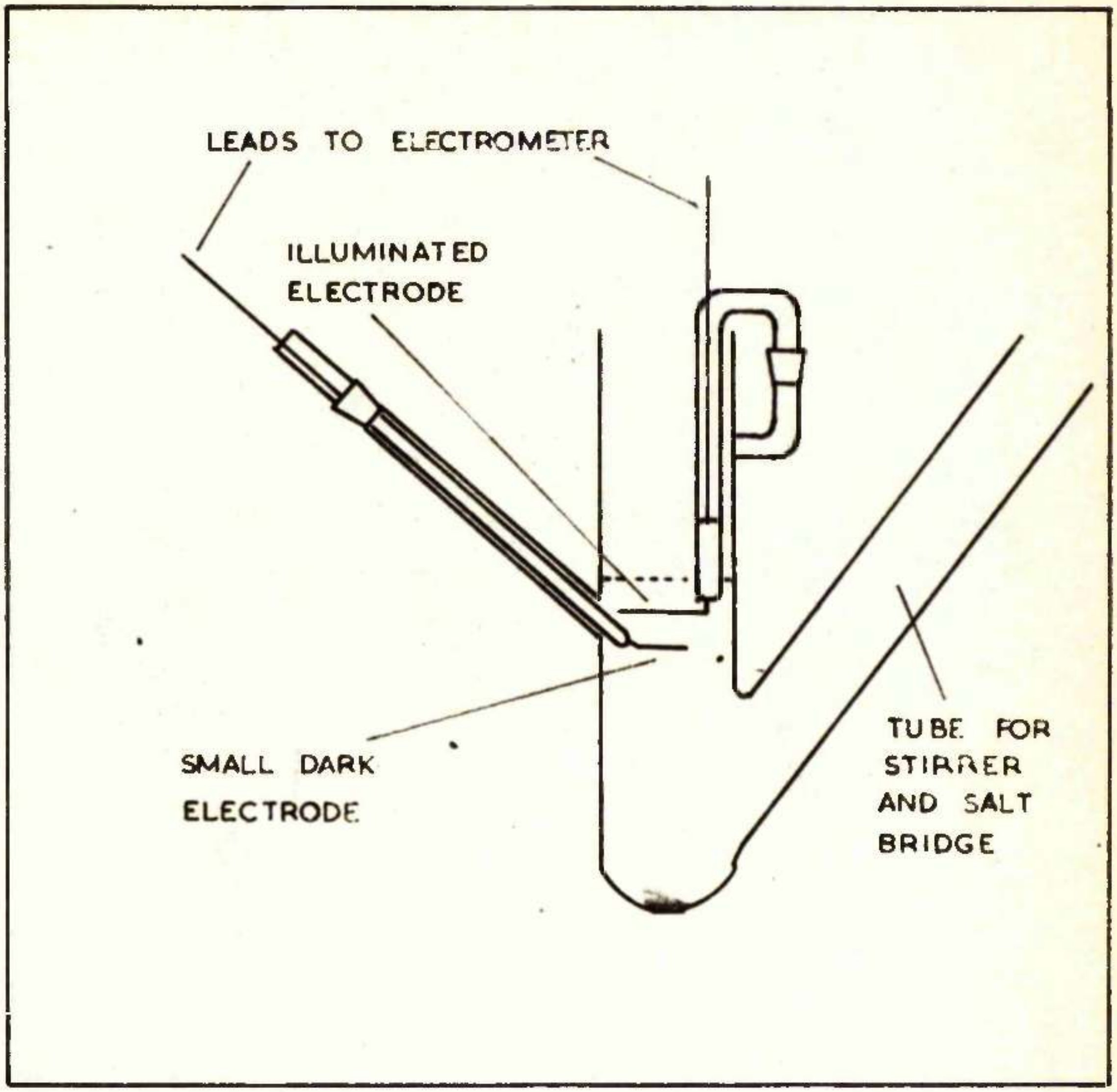
The form of the cell finally adopted is shown in fig.7. The electrode was irradiated by a beam of light from a G.E.C. 250 watt MED compact source mercury vapour lamp placed vertically above the cell. The beam fell on the electrode after passing directly through the solution, there being no intervening glass or quartz barrier. Situated directly below the lamp was a quartz cell, through which water was passed continuously to act as a heat filter. The electrodes were mounted in B.10 soda-glass air leak units and fitted to the corresponding sockets as shown in fig.7. The sealing of the electrodes into the glass at first presented some difficulty, since spurious E.M.F.'s arose through capillary seepage between the platinum and the glass. This problem

FIGURE 6.



ORIGINAL CELLS USED FOR PHOTO-VOLTAIC INVESTIGATION.

FIGURE 7.



FINAL FORM OF CELL USED FOR PHOTO-VOLTAIC INVESTIGATION was finally solved by using sealing glass and testing for leaks under vacuum by means of a high voltage discharge. Connection from the electrodes to the electrometer leads was by means of a pool of mercury in the bottom of the electrode tubes.

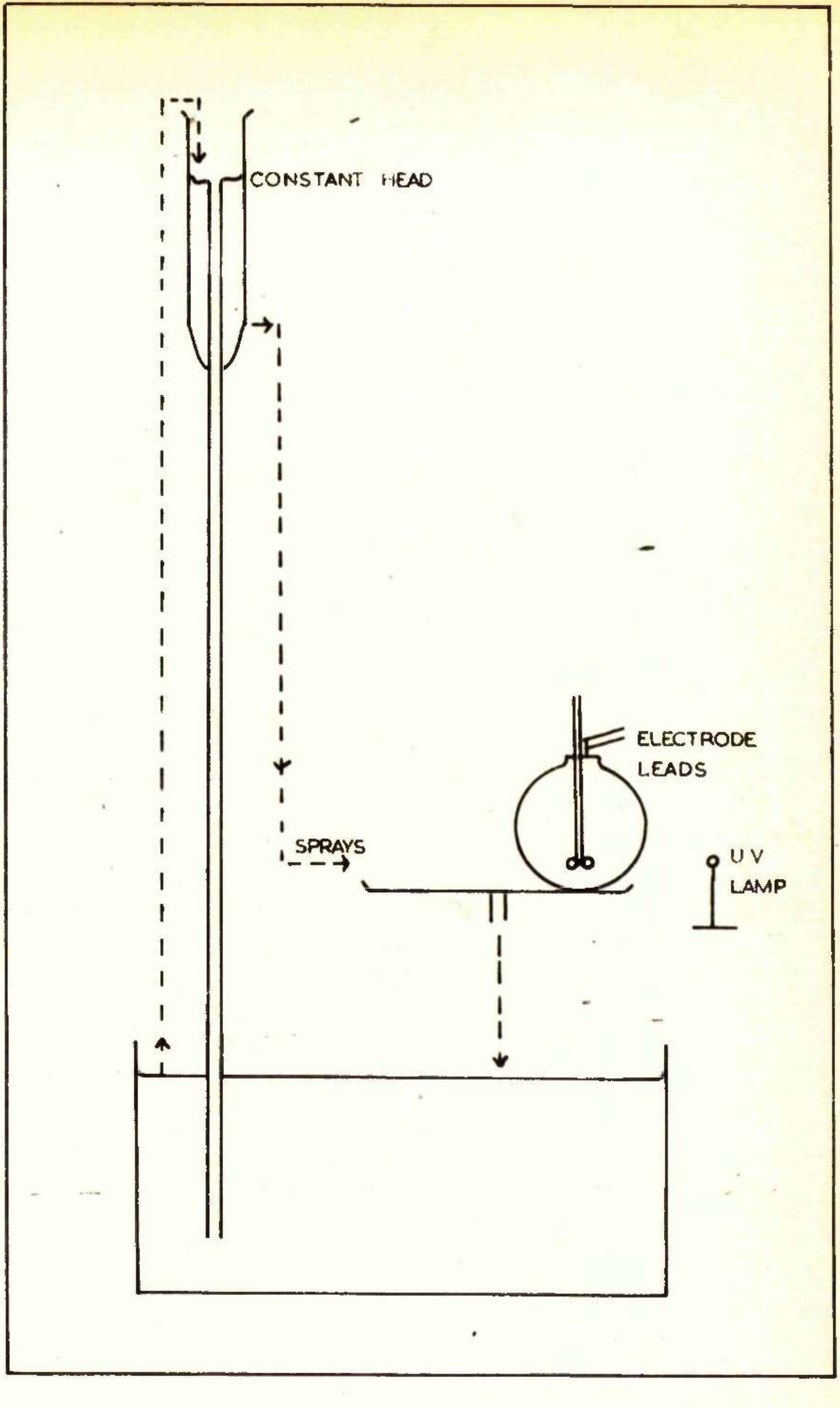
The large side-arm of the unit was used to allow for the insertion of a stirrer, and for a salt bridge to a calomel electrode, which was subsequently used as reference electrode in preference to the small un-illuminated platinum electrode.

The cell and its contents were maintained at 20°C by insertion, up to solution level, in a thermostatted water tank.

Apparatus for following redox potential and pH changes during irradiation.

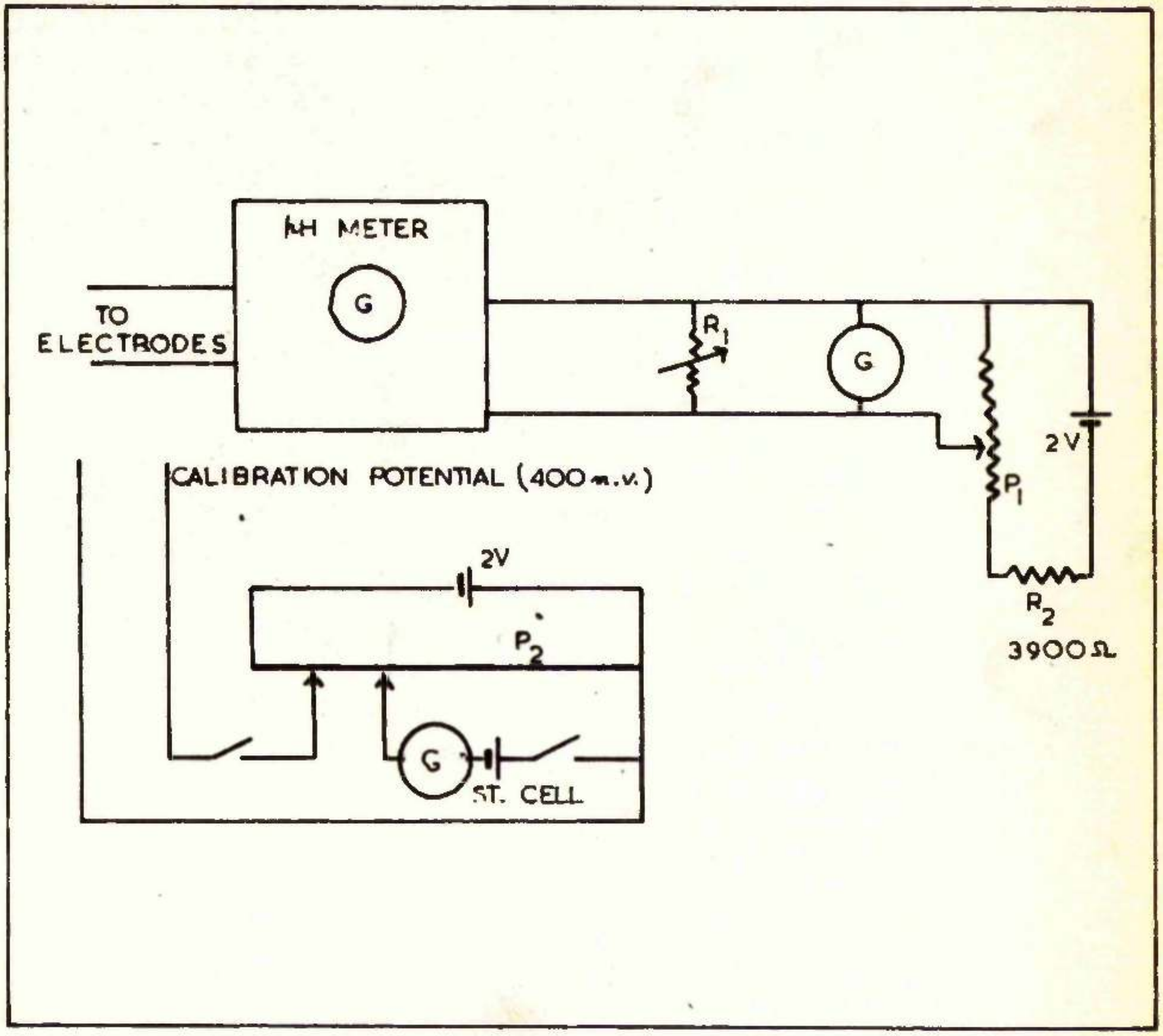
The layout of the apparatus and circuit is shown in figs.8&9. The apparatus consisted essentially of a one-litre Pyrex flask with three sockets, in one of which was inserted a stirrer to ensure adequate mixing of the solution. The flask was mounted in front of a S.500 Hanovia mercury vapour lamp, which was unfiltered. It was maintained at 20°C by being sprayed with thermostatted water containing a little Lissapol N.D.B. as

FIGURE 8.



IRRADIATION APPARATUS.

FIGURE 9.



CIRCUIT FOR MEASURING REDOX POTENTIAL.

wetting agent.

The electrodes consisted of a glass electrode wound round with platinum wire. This close contact reduced the resistance of the cell. In view of a possible photo-voltaic effect, the electrodes were shielded by a tube of cobalt-blue glass to cut off any radiation, penetrating through the solution to the electrode. The tube was perforated at the rear to ensure adequate mixing of the solution in the electrode area.

Leads from the electrodes led to a Pye Universal pH meter, through which the potential across the electrodes was measured.

Measurement of the redox potential and pH of samples withdrawn were made using a Cambridge pH meter. The redox electrode consisted of a spiral of platinum wire sealed into soda glass, sealing glass being used at the joint to obviate spurious potentials caused by leakage. The pH was registered by a glass electrode, using as reference electrode a dip-type calomel.

Standardisation and calibration.

In order to make full use of the sensitivity of the galvanometer, it was necessary to find the range of potential produced by the ferric/ferrous system under investigation. This was found in the following manner.

A solution of ferrous chloride in hydrochloric acid was available. The method of preparation was such that the total iron concentration to chloride concentration was 3/1. The solution was kept under nitrogem.

The analysis of the solution was :-

Ferrous iron	0.1707 M		
Ferric iron	0.0015 M	Chloride ion	0.5183 M
Total iron	0.1722 M		

To one litre of 1.3 x 10^{-3}M ferric chloride solution was added 10 mls. of the ferrous chloride solution, run in from a micro-burette in 1 ml. portions, and the potential between the glass electrode and the platinum noted on the pH meter.

From the known molarities of the solution, the ratio of ferric to ferrous iron was calculated. Since a 30% reduction is brought about during irradiation, the minimum ratio of Fe^{3+}/Fe^{2+} was taken as 2:1. This was found to correspond to an E.M.F. of about 500 m.v. on the pH meter. The upper limit of Fe^{3+}/Fe^{2+} was infinity at time zero. A measurable limit of 800 m.v. was, however, decided upon, and the circuit was calibrated to read from 400 - 800 m.v.

The sensitive galvanometer in series with the electrometer unit had a full scale deflection for 20 m.v. The electrometer unit was so constructed that an applied potential produced a current in any external circuit of 1 ua/m.v. The internal resistance of the unit was so high that a resistance of 10,000 ohms in the external circuit had no appreciable effect on this current. Thus, in order to have a full scale deflection between the range 400 - 800 m.v., it was necessary to apply a potential of 400 m.v. in the opposite sense across the galvanometer, and the value of R_1 had to be adjusted to bring the total resistance of the galvanometer + R_1 in parallel to about 50 ohms. R_2 was adjusted to give, in series with P_1, a current of about 400 ua from an accumulator.

These values were calculated and the circuit set up. It was found necessary to use a high resistance potentiometer (30,000 ohms) to prevent current drain through the circuit, as was found with a Cambridge potentiometer.

With the circuit as shown in Fig. 9, a potential of 400 m.v. from a potentiometer was applied to the electrometer unit, and the galvanometer zeroed by means of the "Zero Control" on the electrometer unit. P_1 was then adjusted to bring the galvanometer again to zero.

Potentials ranging from 400 - 800 m.v. were then applied to the electrometer unit and the galvanometer reading noted. A straight line graph was obtained, connecting potentials with scale readings :-

Potential = 400 + 20.55s.

In order to read the pH and redox potential in quick succession, it was necessary to calibrate the pH reading in terms of m.v. This was done by using two buffers of pH 4.00 and 7.01 and plotting pH against m.v. The slope of the curve 57.8 m.v./pH agreed well with theory, but, due to variation in the glass electrode constant, the calibration had to be repeated frequently.

Analysis.

The hydrolysis of the solution was followed by observing the change in optical density during the run. This was measured on a Hilger "Spekker" absorptiomer, on samples taken during the run, using Ilford 601 filters (peak transmission 430 mu.)

Ferrous iron. This was estimated colorimetrically with the reagent 2-2' dipyridyl, the solutions containing ammonium acetate/sulphuric acid buffer to control the pH to give maximum colour, and ammonium fluoride to complex ferric iron present. 2 ml. samples of the test solution were placed in 20 ml. graduated flasks containing the indicator/buffer/fluoride mixture in the ratio 2/5/2 and the total made up to the mark with distilled water. The colour was allowed to develop for 24 hours, after which it was estimated in 4 cm. cells on the "Spekker" using Ilford 604 filters (peak transmission 515 mu). The concentration of ferrous iron was then read from a conversion graph, previously drawn up by using solutions of known ferrous iron content.

All glassware was washed in an NaOH/alcohol mixture to remove any grease, and hydrochloric acid to remove any traces or iron. The flasks were well rinsed, finally with distilled water prior to drying.

The platinum and glass electrodes were left in dilute hydrochloric acid to remove any film which might have been formed in the previous run. The acid strength was N/100 so as not to injure the glass electrode. The electrodes were placed in distilled water for an hour before the run.

The electrometer unit was left switched on for at least an hour before using to allow it to stabilise.

The U.V. lamp was also switched on, the irradiation flask being kept shielded for half an hour before the run.

The galvanometer was zeroed using a potentiometer as described above. The electrodes were then inserted in the flask and connected up to the electrometer unit.

The ferric chloride was added and a sample of the solution immediately withdrawn. The optical density and pH were found on the "Spekker" and Cambridge pH meter respectively.

The shield was withdrawn from the flask and this taken as zero time. Samples were withdrawn at suitable times for estimation of optical density, ferrous iron, pH and redox potential. The galvanometer deflection was also noted.

In the estimation of ferrous iron, 10 ml. samples were used over the first hour of the run, but after this period, 2 ml. samples sufficed.

Materials.

Water. The water used was distilled from an all-glass Pyrex still of Automatic design, manufactured by L.V.D. Scorah of Birmingham, and was found to give identical results to that obtained from double distillation from alkaline permanganate.

Iron stock solution. Earlier workers investigating hydrolysis phenomena in iron solutions, prepared by dilution of a concentrated stock solution, found that their results depended in a very marked way on the age and history of the stock solution. To avoid such difficulties, Lamb and Jacques[39] prepared their dilute solutions by the addition of a small weighed portion of the anhydrous salt to pure water.

An irreproducibility with regard to the photosensitivity was found in the work of Purdon when the solutions were prepared from a concentrated iron stock solution. A method, however, which was found to give entirely satisfactory reproducibility in the photoreduction was to melt the solid A.R. ferric chloride ($FeCl_3.6H_2O$), melting point 39°C., in a small tube fitted with a ground glass cap, maintaining it at a temperature of 45°C. for thirty minutes and then slowly cooling it to 20°C. The ferric chloride remained liquid, presumably supercooled, and the desired quantity, normally 0.1 ml. per 500 mls. of solution was measured with an "Agla" mictometer syringe into the desired quantity of water. When not in use the stock was allowed to resolidify.

Preparation of solutions. Solutions of 1.3×10^{-3}M ferric chloride were prepared by adding 0.1 ml. liquid melt dropwise from the syringe with constant stirring into 500 mls. of distilled water. This solution had a pH of 3.05. For work on lower pH values, the ferric chloride was added to an appropriately dilute solution of hydrochloric acid. Stock solutions of the acids were prepared from the A.R. materials.

When it was desired to have substrate present, this was added to the distilled water prior to the addition of the iron.

Since the rate of addition of the ferric chloride salt and the rate of stirring had, as found by Purdon, an effect on the experimental results, standard procedure was adhered to throughout. In particular the melt was added from the syringe as rapidly as possible, since hydrolysis tended to be initiated immediately in solutions of low concentration which were formed during addition of the melt, were this added too slowly.

All other materials used in the investigation were of A.R. grade.

RESULTS.

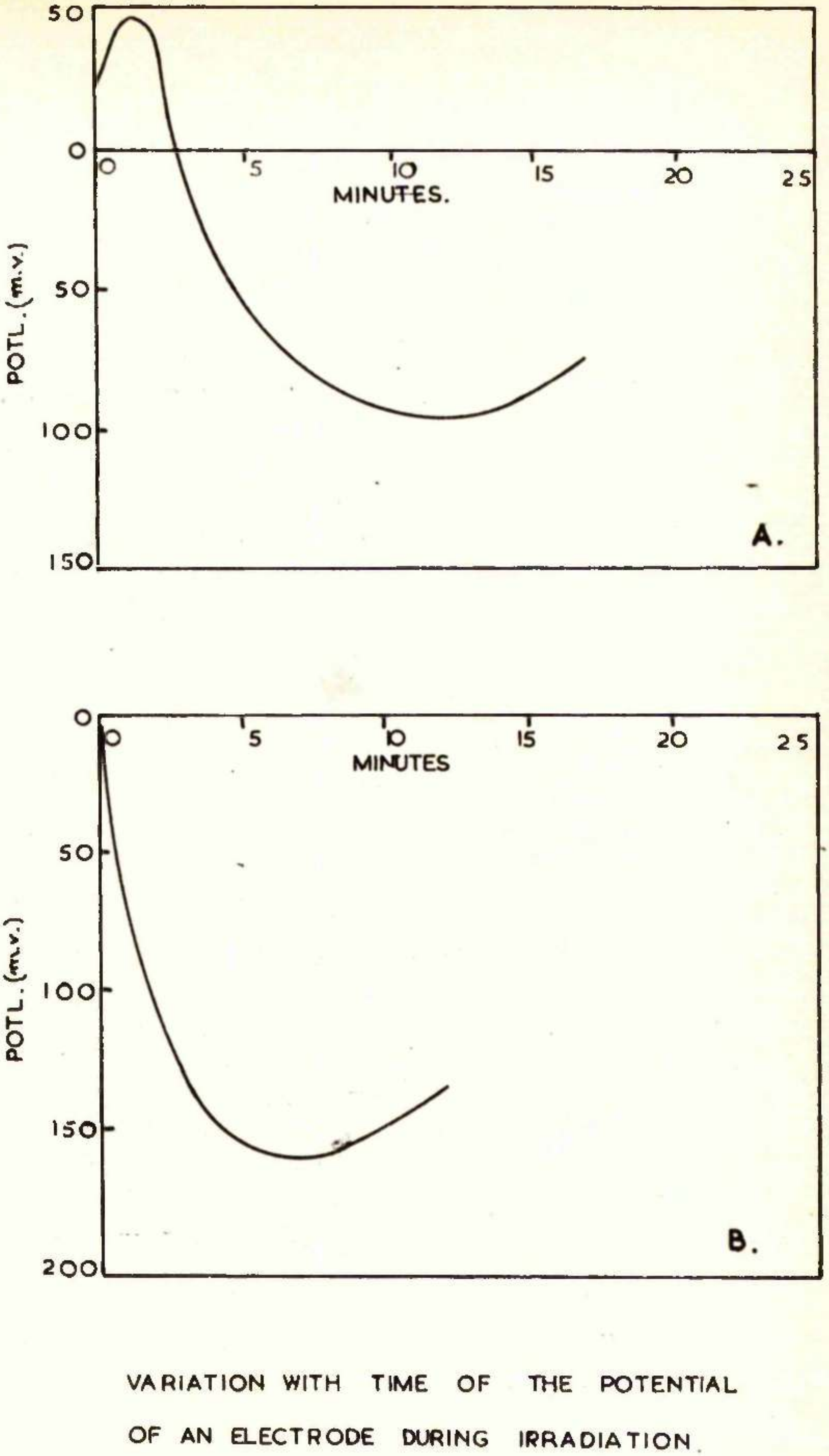
The photo-voltaic effect.

Using the two cells shown in Fig. 6, no reproducible results were obtained, although the photo-voltaic effect was exhibited most markedly as shown in Fig. 10 which gives two curves from a series of runs. In general, from the moment of illumination, the potential of the electrode rapidly changed by approximately 50 m.v./minute.

It was observed that, if between runs, the cell and electrode were rinsed out in dilute HCl, followed by distilled water, then the general shape of the curve was as in Fig. 10B. If however distilled water only was used for rinsing, then the shape of the curve was as in Fig. 10A. The maximum of the positive portion of the curve varied and the time at which zero potential was again reached varied from 2 to 5 minutes from the beginning of irradiation. Introduction of stirring made all potentials drift to zero, the rate of drift depending on the rate of stirring.

The electrodes, if allowed to stand for some time in the solution, acquired a distinctly visible golden sheen. This was thought to be due to a layer of (colloidal) iron hydroxide.

FIGURE 10.



VARIATION WITH TIME OF THE POTENTIAL OF AN ELECTRODE DURING IRRADIATION.

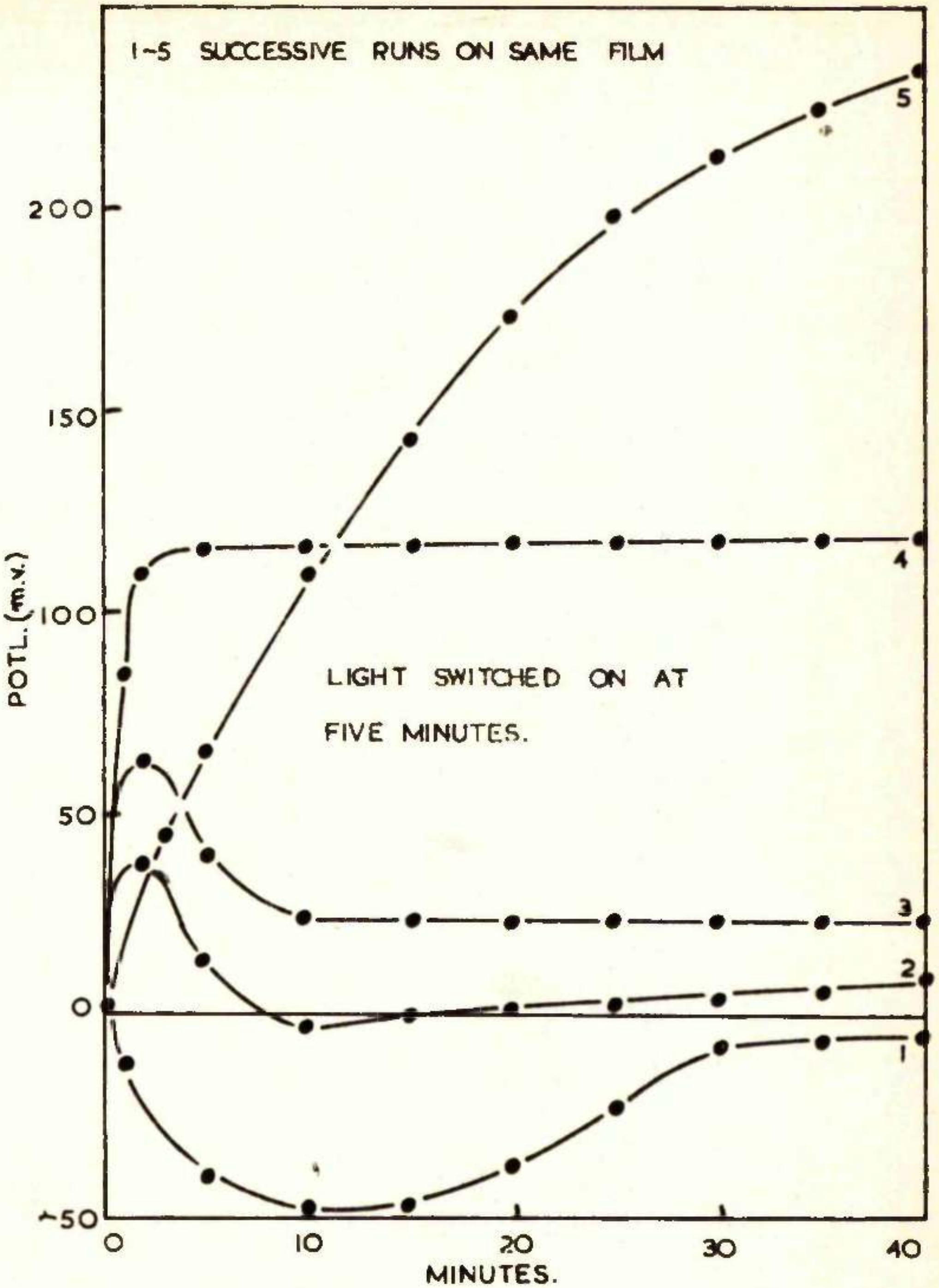
It seemed likely that such a layer, though not visible after 30 minutes irradiation, was nevertheless present to some extent on the surface of the platinum. Washing with hydrochloric acid would remove it, whilst washing with water would not, and on irradiation this layer would interfere with the normal photo-voltaic effect.

That a positive E.M.F. was obtained on irradiation was interesting since this would tend to indicate the formation of iron of valency greater than three on the electrode surface.

A more thorough investigation of this positive E.M.F. was carried out using the modified cell described above.

Initial runs were carried out with both electrodes in the cell, so that the potential developed was that between an illuminated and an unilluminated small electrode. In these runs the stirrer was not running. The results are shown in Fig. 11. Curve (1) is for the first run with both electrodes cleaned in hydrochloric acid, and subsequent curves are for subsequent runs in which there was no cleaning of the electrodes in acid, though they were rinsed with distilled water. In the course of these experiments they had acquired a distinctly visible golden sheen, noticed in the previous experiments mentioned above.

FIGURE II.



ILLUMINATED ELECTRODE VERSUS SMALL PLATINUM ELECTRODE.

It was found that this film built up, irrespective of illumination, to a visible extent after about three days immersion in the ferric chloride solutions, provided the solution was renewed each day. If the ferric chloride solution was not renewed each day, there was no visible growth of the film, even after the elapse of a week, but on subsequent renewal of the solution, development of the film was observed.

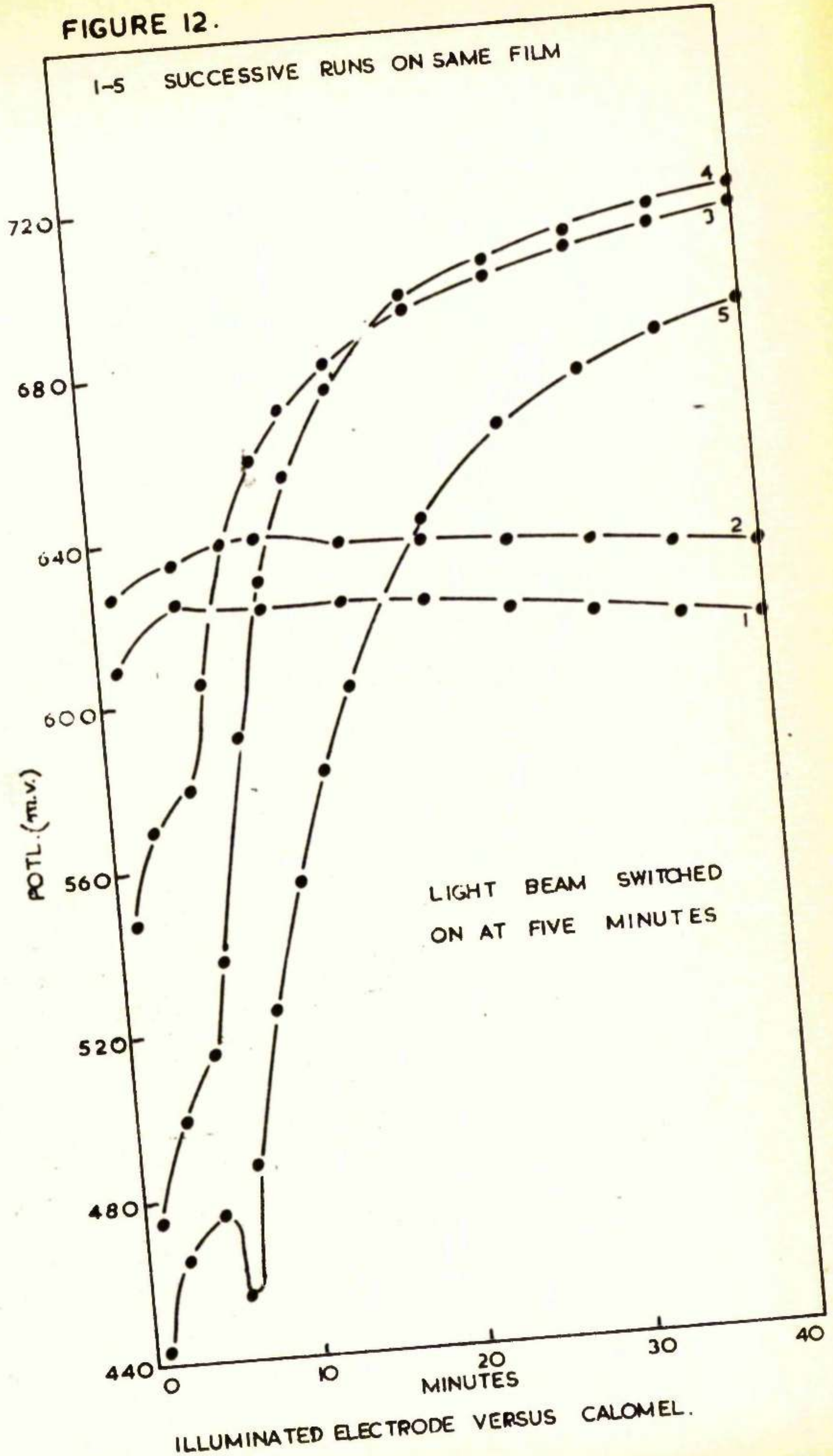
On order to facilitate interpretation of the results, it was then decided to measure the potential of the illuminated electrode against a saturated cell, again without the stirrer running. Any change in potential would now be due to some change at the illuminated electrode, without the possible complicating effect of the small electrode, which by this time had also acquired a film. A series of results is shown in Fig. 12.

A ¼" beam of light was used for the above runs. This was now replaced by a ¾" beam. The results are shown in Fig. 13.

In solutions of potassium chloride of various concentrations from saturated to 0.01M, the potential on the electrode was found to remain steady on irradiation.

The addition of small quantities of hydrochloric

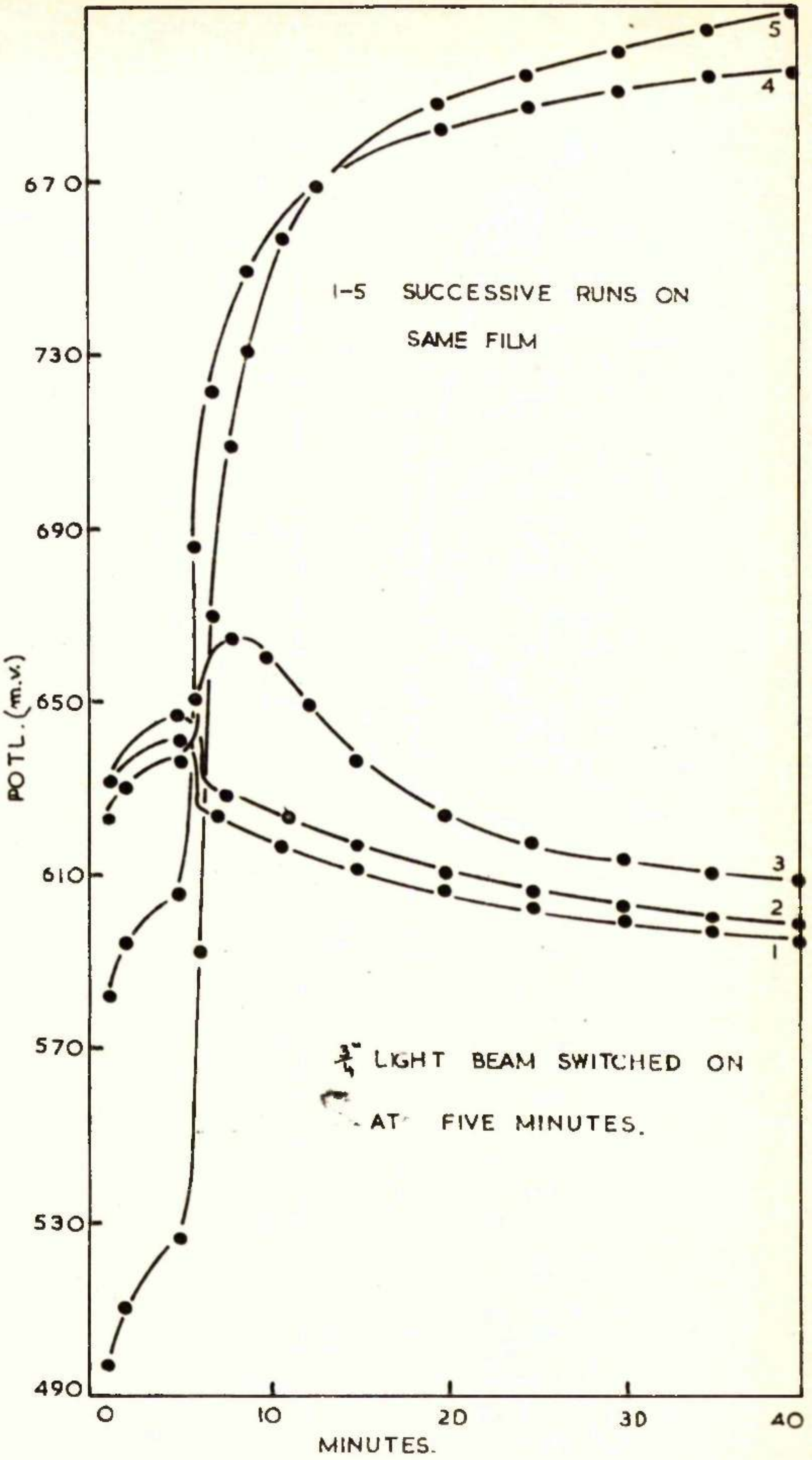
FIGURE 12.


1-5 SUCCESSIVE RUNS ON SAME FILM

LIGHT BEAM SWITCHED ON AT FIVE MINUTES

ILLUMINATED ELECTRODE VERSUS CALOMEL.

FIGURE 13.



ILLUMINATED ELECTRODE VERSUS CALOMEL

acid to any solution in the cell was found to cause a large increase in potential, even without irradiation. A fall of similar magnitude was obtained on addition of small quantities of sodium hydroxide. As this indicated a pH dependance of the electrode system, it was decided to carry out an investigation of this effect over a wide pH range (from 2 to 12).

Solutions having the required acidity were prepared by stirring into a beaker containing 500 mls. of distilled water, quantities of either 0.1N hydrochloric acid or 0.1N sodium hydroxide solution. The pH was adjusted, using these solutions, by measurement of the pH of the resulting solution in the beaker with a glass electrode/calomel system connected to a Pye Universal pH meter. It was found in practice that the solutions were quite stable as regards pH without the necessity of adding buffer solution. The water used had a pH of 5.6, presumably due to dissolved carbon dioxide.

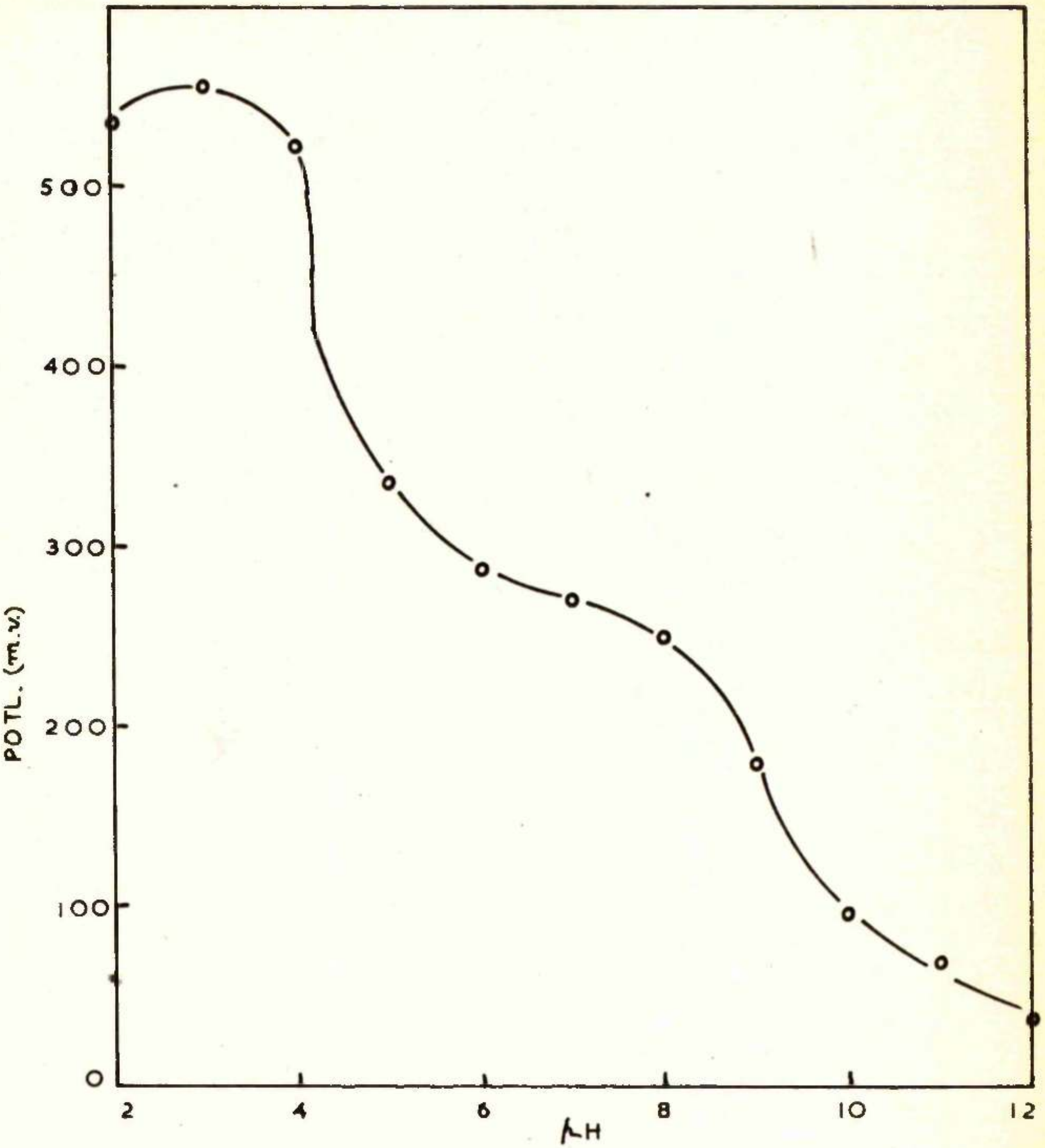
Without irradiation, the electrode with its film attained an equilibrium potential, this potential varying with pH and being quite reproducible with regard to each individual pH value. Normally thirty minutes was allowed for the equilibrium value to be reached, since originally a slight upward drift of potential was noted duringthis period of time after introducing the solution into the cell. This drift was later found to ba a temperature effect, since the water used for preparing the solutions had not normally been thermostatted before use. When this precaution was adopted, it was found that equilibrium was reached within one minute, i.e. for all practical purposes instantaneous.

The results are shown in Fig. 14 where it is seen that there are two points of inflexion on the graph. These were observed for every series of runs undertaken. The average slope of the curve is seen to follow that of a glass electrode.

The above run was repeated, except that at each pH, the electrode was irradiated for thirty minutes and the resulting rise or fall in potential from the equilibrium potential before irradiation noted. The results are shown in Fig. 15, where it is seen that below pH 3, there is a rise in potential on irradiation, whilst above pH 4 there is a fall.

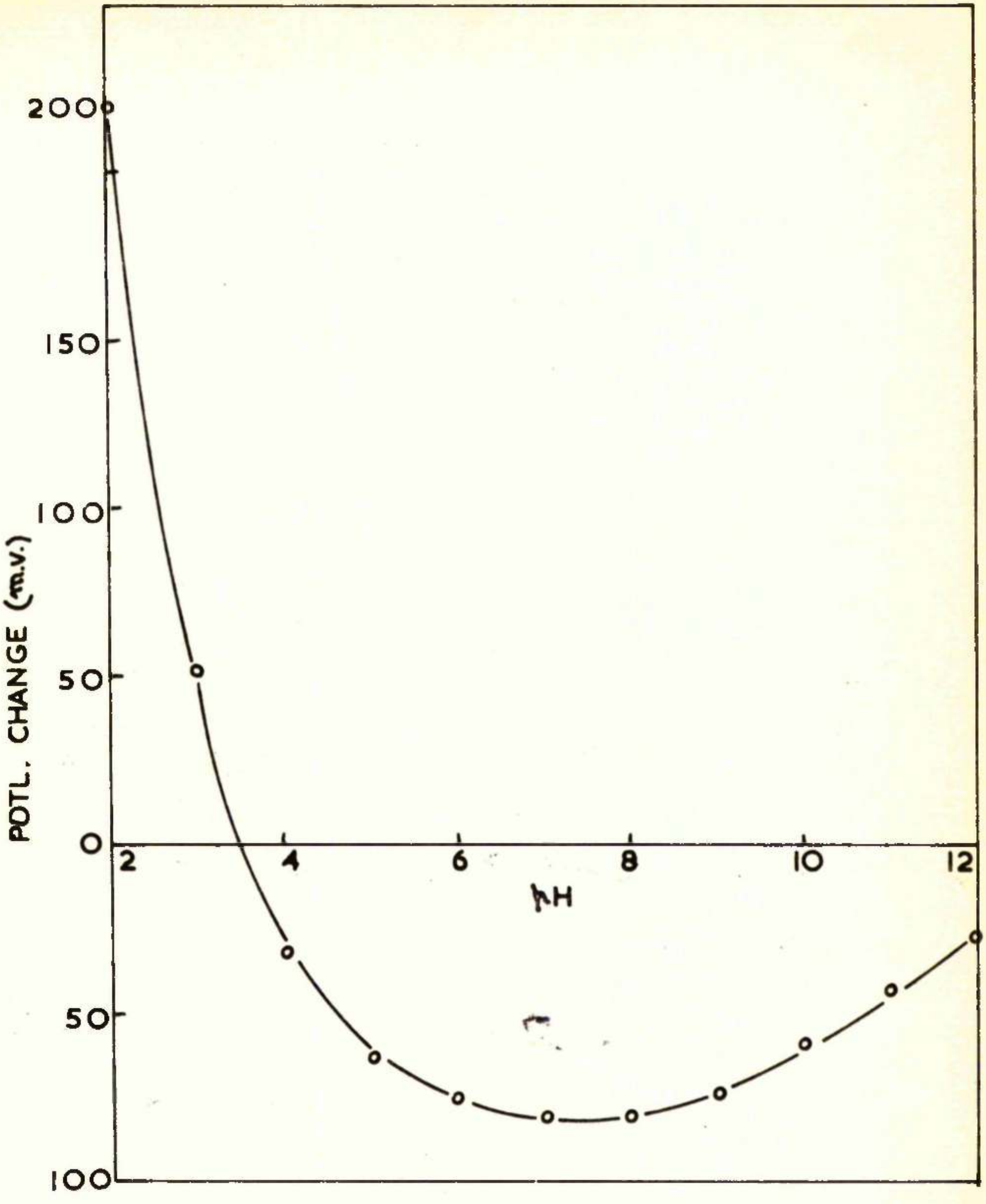
The effect of solutions of hydrogen peroxide was tried on the electrode system without irradiation, since hydrogen peroxide is thought to be an intermediate in the

FIGURE 14.



EQUILIBRIUM POTENTIAL IN A SOLUTION OF VARIOUS ACIDITIES.

FIGURE 15.

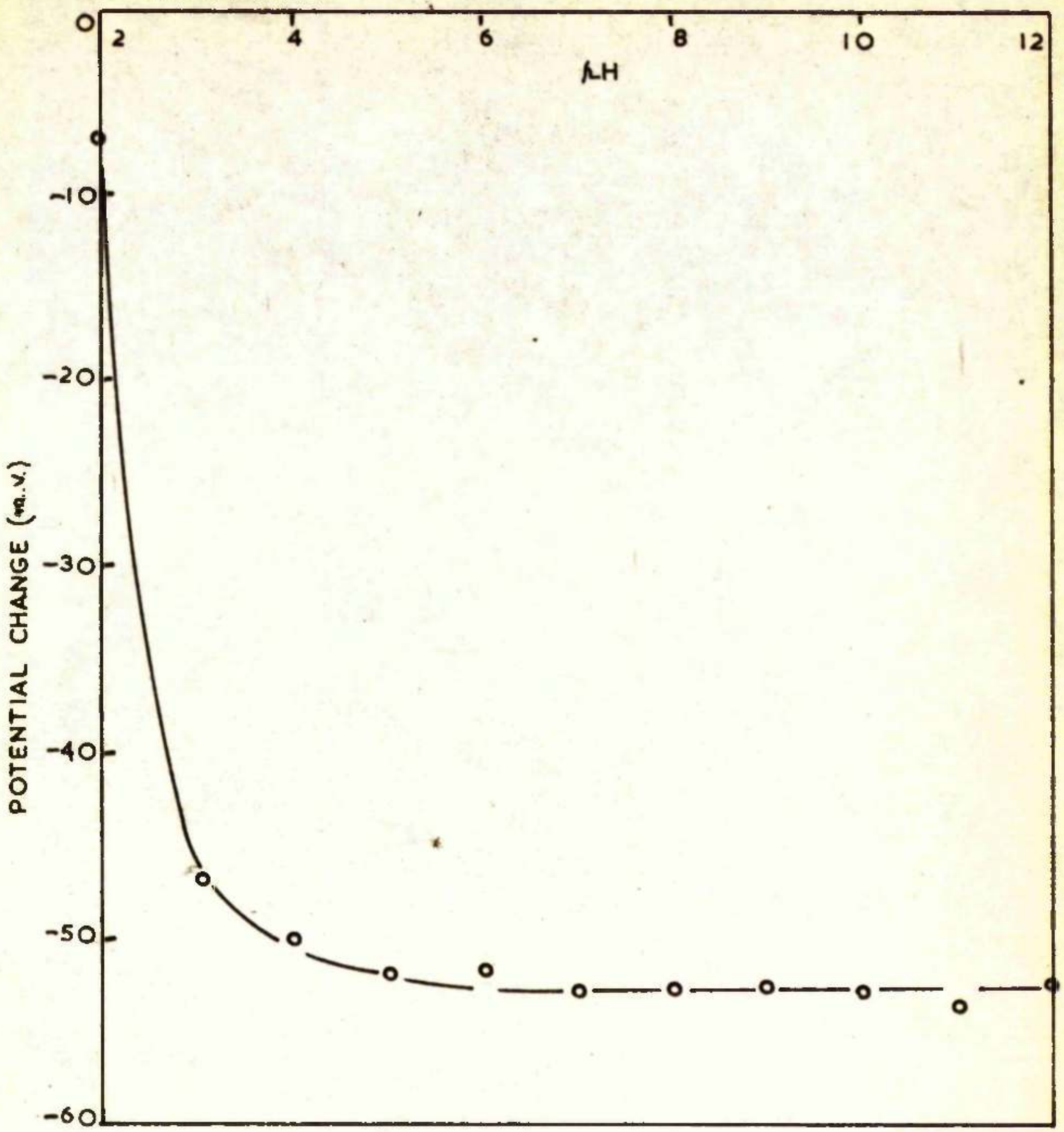


POTENTIAL CHANGE OF FILM ON IRRADIATION IN A SOLUTION OF VARIOUS ACIDITIES.

photo-reduction of ferric chloride solutions, and it was thought that the ferric hydroxide film could act as an electrode, sensitive to the perhydroxyl ion of perhydroxyl free radical.

The procedure adopted was similar to that for the above two runs, to obtain a solution in equilibrium potential at a known pH. 0.5 mls. of 0.0015M hydrogen peroxide were then added to give an initial concentration of peroxide in the solution in the reaction cell of 3.75×10^{-6}M. The potential was found to fall to a steady value, after which it slowly rose again. The curve of potential change against pH is shown in Fig. 16. It will be noted that the value is reasonably constant after pH 5. It was also noted during the run, that at pH 2, the steady value was reached after 4 minutes and that after twenty minutes the value of the potential had returned to that at which it commenced before the addition of the peroxide. At higher pH's however, 30 minutes were required for the steady value to be attained, and return to the original equilibtrium value took one to two hours. It was therefore assumed that the peroxide was decomposing more rapidly in the solutions of low pH, accounting for the much smaller drop in potential observed.

FIGURE 16.



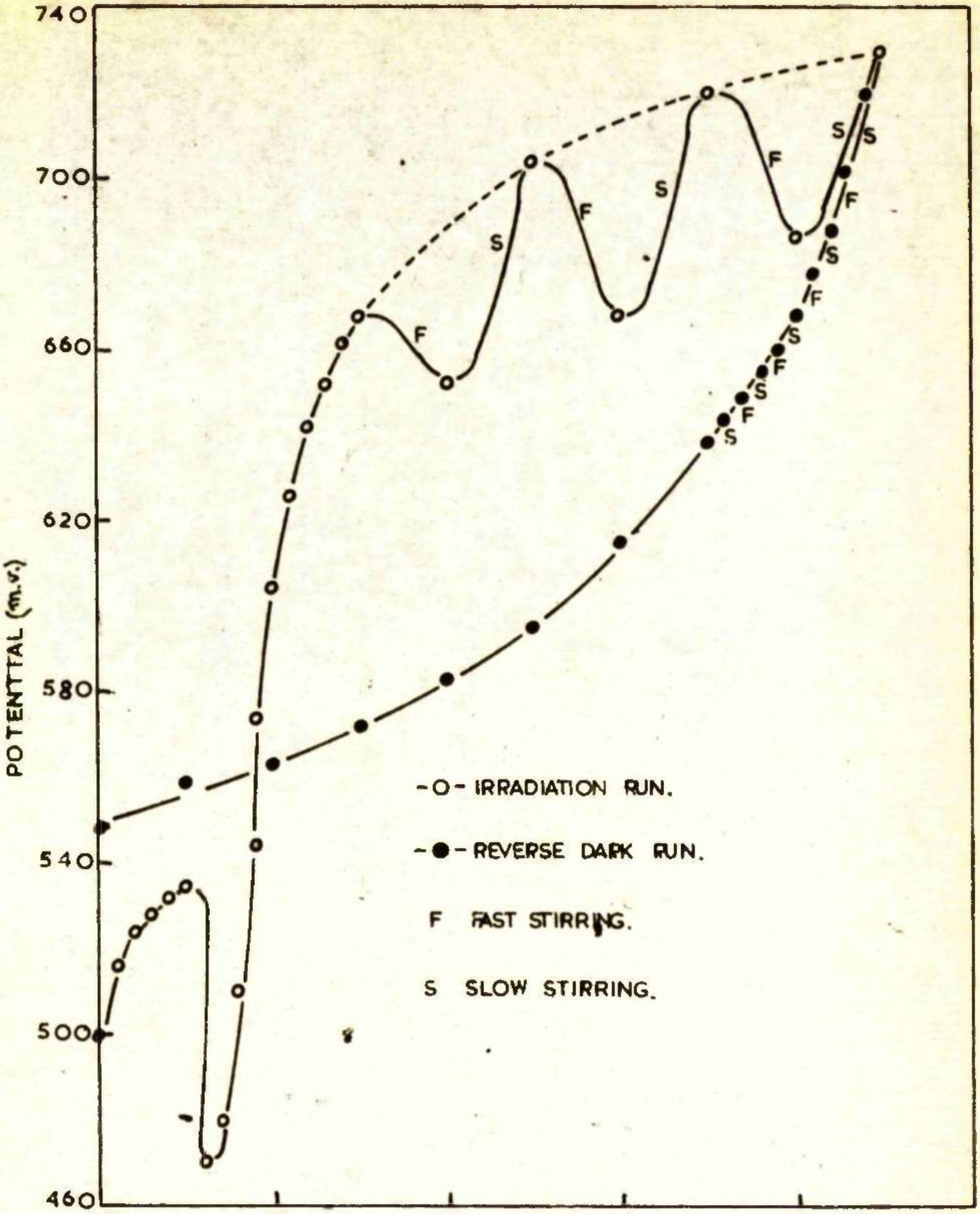
CHANGE IN EQUILIBRIUM POTENTIAL IN PRESENCE OF HYDROGEN PEROXIDE.

This effect of peroxide gave a clue as to the cause of the initial drop in potential observed when the lamp was just switched on to illuminate the electrode in ferric chloride solutions. This drop had not been observed when acid or alkali solutions formed the media in which the electrode was immersed.

To gain more information on this point, an irradiation run was carried out, using ferric chloride as solution. The irradiation was continued for forty-five minutes with stirring after which the potential drop in the absence of light was observed during a further forty-five minutes. During the first fifteen minutes of irradiation, stirring was at a very slow speed, and thereafer it was varied from very slow to very fast speed at five minute intervals, to investigate the effect of fast and slow stirring of the solution. The "reverse run" in the absence of light also had alternation of stirring speed at five minute intervals. The result is shown in Fig. 17. On repeating the experiment in acid and alkali solutions it was noted that stirring produced no appreciable effect.

A film was built up on a glass electrode by immersing the electrode in a solution of ferric chloride for three

FIGURE 17.



EFFECT OF STIRRING ON POTENTIAL IN FERRIC CHLORIDE SOLUTION.

days, the solution being renewed each day. The potential developed between the electrode and a dip-type calomel electrode in buffer solutions of 4.0, 7.05 and 9.14 was measured before treatment of the electrode and on the subsequent three days whilst the film was building. The results are shown in Fig. 18, where it is seen that the film had a negligible effect on the normal pH response of the glass electrode, though the film was thick enough to be visible to the naked eye.

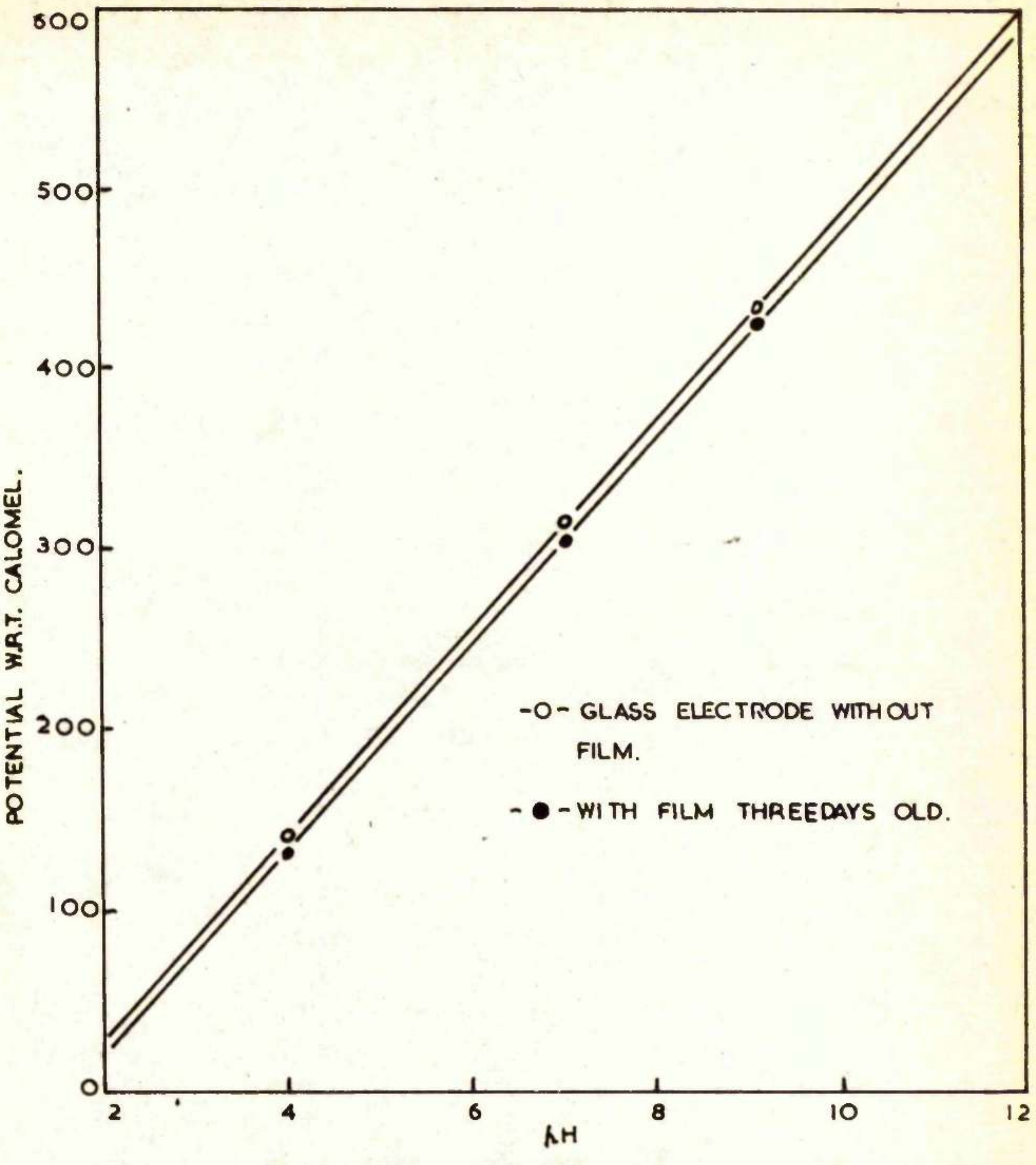
Redox potential and pH change.

In the first set of runs, a one-hour total irradiation period was tried, during which samples were taken of optical density, pH, redox potential and ferrous concentration at 2,5,10,20,30,45 and 60 minutes. A record of the difference in potential (referred to as Pt/glass) between the platinum spiral and the glass electrode were also made in this period. The platinum electrode was found to be positive with respect to the glass electrode.

With these results established, the irradiation run was increased to six hours, readings being taken half-hourly.

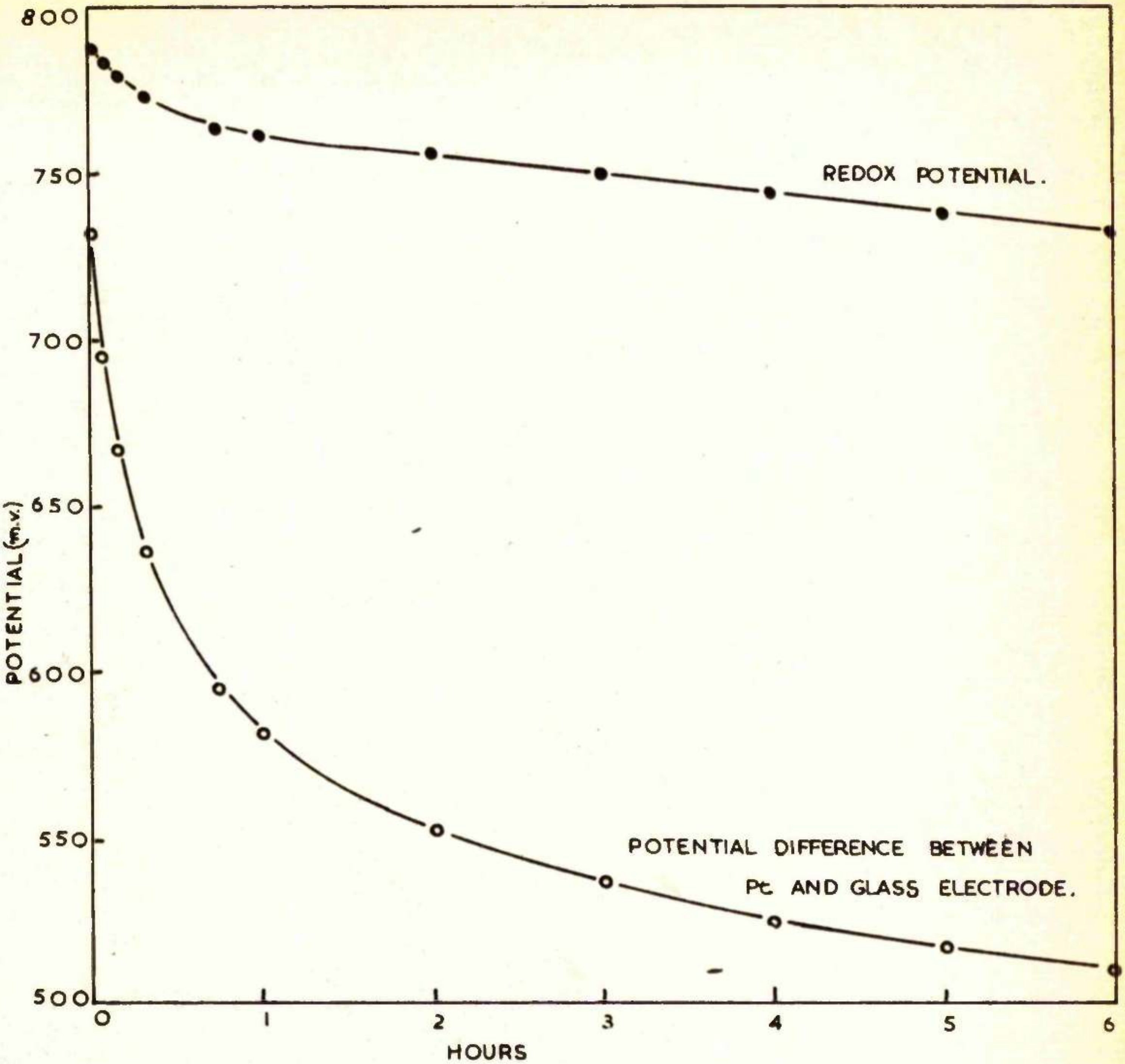
Fig. 19 shows the redox potential versus calomel in

FIGURE 18.



EFFECT OF FILM ON GLASS ELECTRODE.

FIGURE 19.



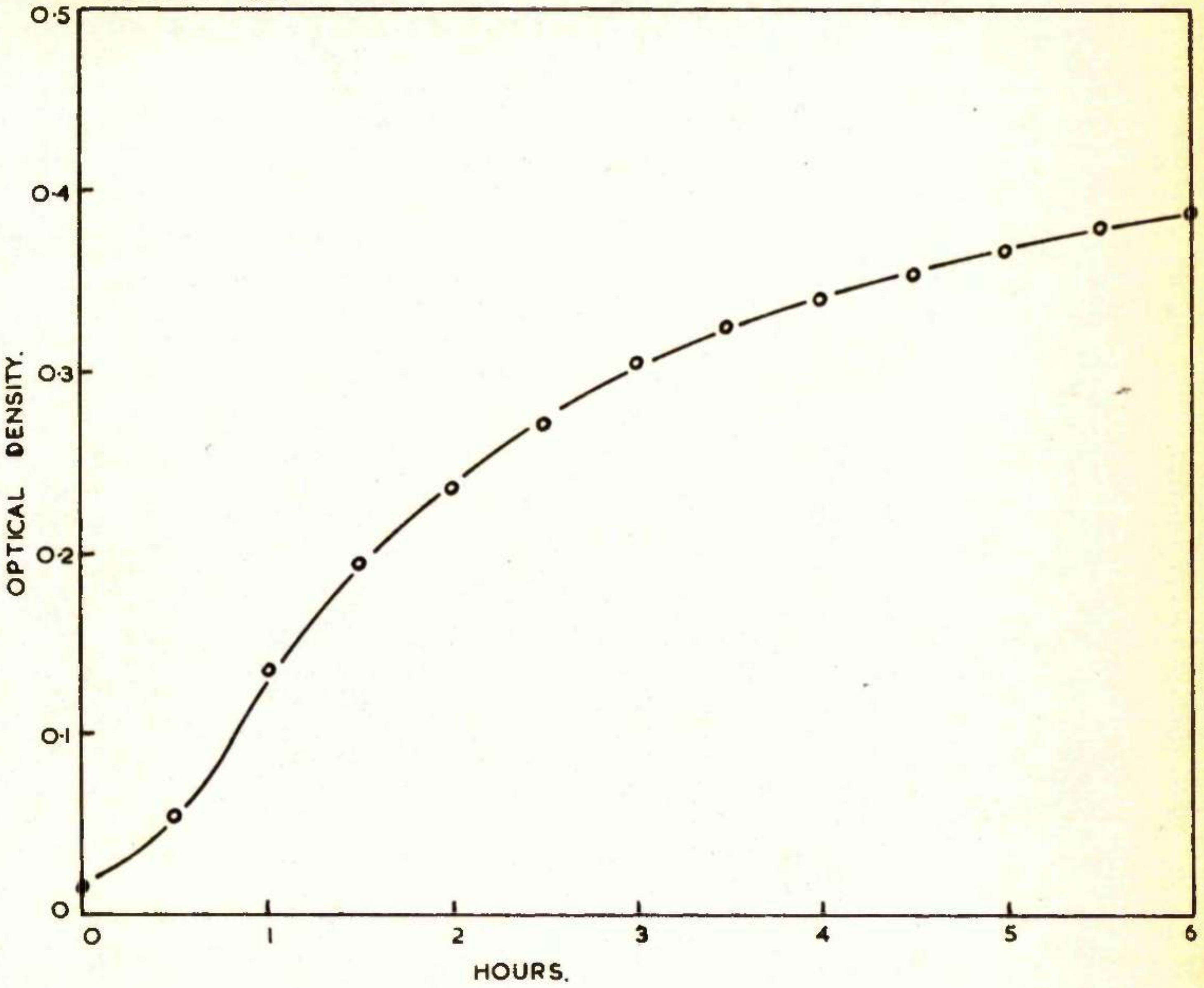
VARIATION OF POTENTIAL WITH TIME.

curve (a) and versus Pt/glass in curve (b). The readings of the Pt/glass were highly reproducible with a mean deviation of less than 1%. At the time zero, the potential is infinite (theoretically). As irradiation proceeds, the increase of ferrous iron leads to the setting up of definite potentials. Due to the difficulty of withdrawing a sample at a precise moment, and to the subsequent time taken to measure the redox potential, the initial value recorded was not as high as theory would predict. This effect became less evident as the amount of ferrous iron grew. The value of redox potential measured was the value reached after the redox electrode had been standing in the sample for a few minutes. This value was higher than the reading initially recorded on insertion of the electrode in the sample.

Fig. 20 shows the change in optical density of the solution with time. This was very temperature sensitive, and great care was necessary to maintain the temperature at 20°C. The optical density is a measure of the extent of secondary hydrolysis. After 24 hours irradiation, the final value of the optical density was 0.42.

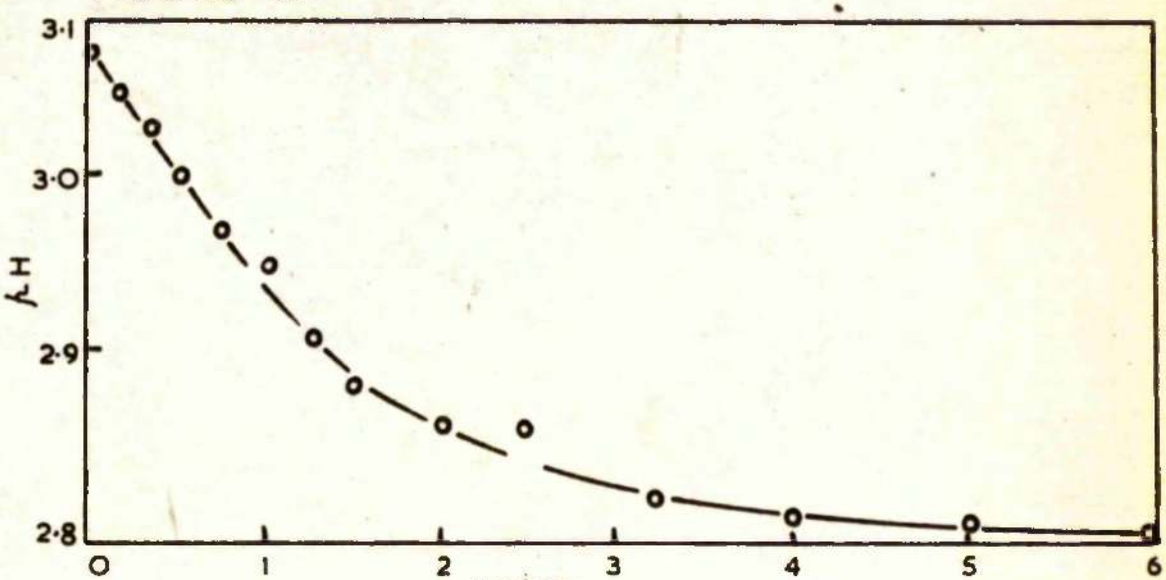
In Fig. 21 the change of pH during a run is shown. This is dependent on the hydrolysis and is thus subject to the same temperature variation.

FIGURE 20.



VARIATION OF OPTICAL DENSITY WITH TIME DURING IRRADIATION.

FIGURE 21.



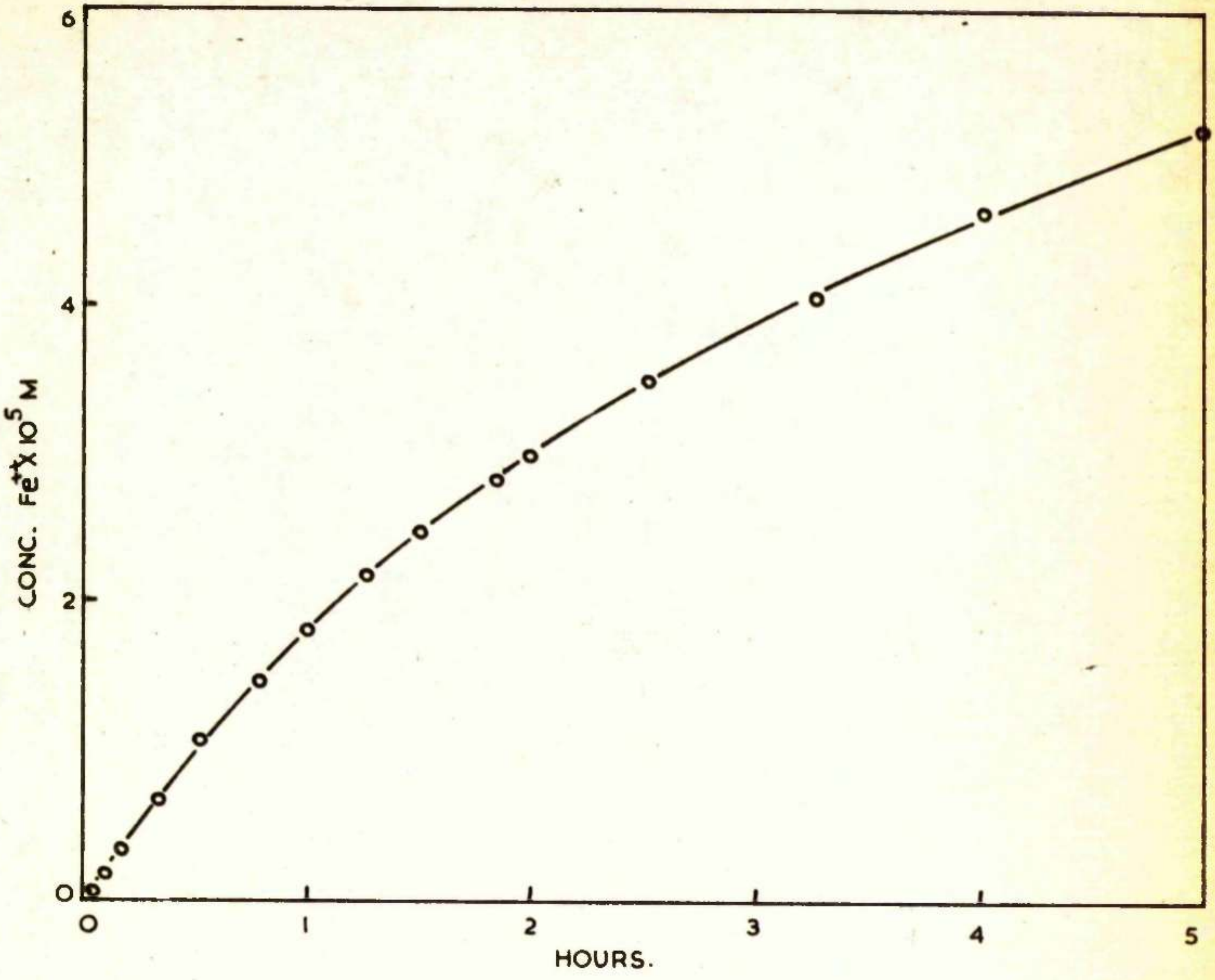
VARIATION OF pH WITH TIME DURING IRRADIATION.

The redox potential and the pH were read on the same sample. The pH was read in m.v. and converted to pH by means of a factor, obtained by measuring the potential between a glass electrode and a calomel in buffer solutions at pH 4.00 and 7.01. pH's could be read to an accuracy of ± 2%. The average pH values were in good agreement with those reported by Purdon. After 11 hours irradiation the pH value was 2.75, which may be regarded as the equilibrium value.

Fig. 22 shows the variation of ferrous ion during irradiation. Although not yet at equilibrium, the value reached indicates that an approximately 30% reduction will be attained at equilibrium, as found by Purdon. The amount of reduction at any given time, will, of course, vary from apparatus to apparatus, as will the other quantities measured.

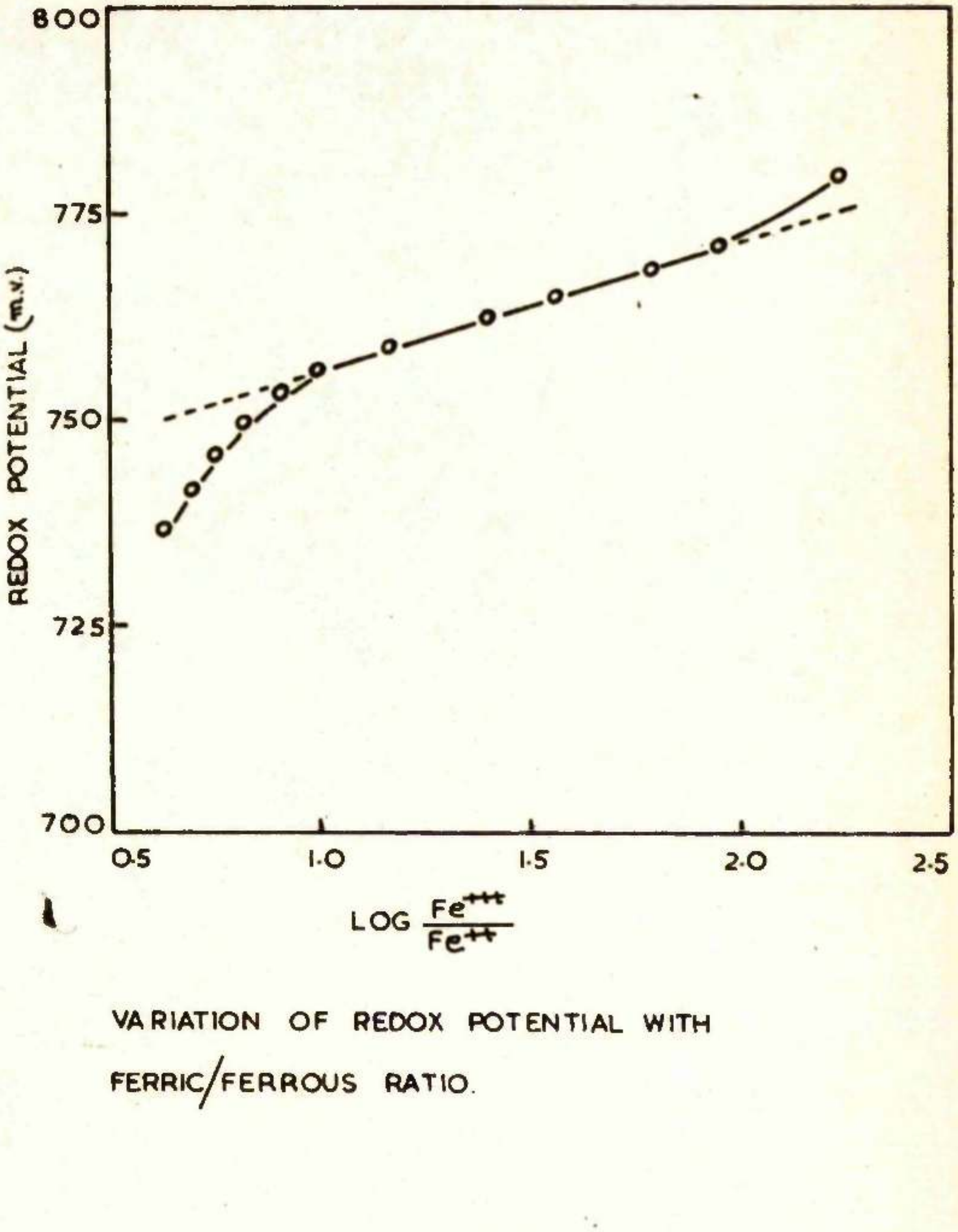
Fig. 23 is a plot of the redox potential against log Fe^{3+}/Fe^{2+}. The ferric concentration was found from the difference between the initial ferric concentration (1.3×10^{-3}M) and the ferrous iron as found by analysis.

FIGURE 22.



INCREASE IN FERROUS ION DURING IRRADIATION.

FIGURE 23.



VARIATION OF REDOX POTENTIAL WITH FERRIC/FERROUS RATIO.

DISCUSSION.

The "photo-voltaic" effect.

It is seen from Fig. 11, that on irradiation, the potential of a clean platinum electrode in ferric chloride solution diminishes. This is likely to be due to the formation near the illuminated electrode, of ferrous ion in solution, causing a potential which is negative relative to the unilluminated electrode. The potential gradually drifts back towards zero, due to ferrous ion diffusing in the solution and reaching the unilluminated electrode.

After a few days, however, when the electrode is not cleaned with hydrochloric acid, but rinsed only in water, an increasingly large positive potential is developed on irradiation. At this stage also the film is becoming visible on the electrodes. It is suggested in explanation that this film consists of iron hydroxide, and on irradiation is activated in such a way that it can reduce the ferric iron in the immediate solution, and be itself oxidised to a higher valency state.

Thus Fe^{3+}(film complex) $\xrightarrow{h\nu}$ Fe^{4+}(film complex) + e^-

and Fe^{3+}(solution) + e^- $\rightarrow$ Fe^{2+}(solution).

Results with the calomel electrode introduced in place of the small unilluminated platinum electrode would indicate that the film contains also some oxide in a lower valency state than three, since as the film builds up, the equilibrium potential in the dark becomes lower on subsequent days. However, the high final potential developed on irradiation still supports the idea that a valency state of iron higher than three is produced.

With the larger beam, there is both a greater initial rate of rise and a greater rise in potential, indicating the formation of an intermediate activated complex before the material on the film reaches the higher valency state.

Since a film built up on a glass electrode causes a negligible change in the hydrogen ion response of the latter, it may be concluded that the film itself is completely pervious to hydrogen ions. For the film to give the pH dependence observed with a glass electrode, however, would demand a constant hydrogen ion concentration on the opposite side of the interface from the solution. As there is no such concentration at the film interface, and as the slope of the graph for pH dependence is of the opposite sign to that of a glass electrode, it seems more probable that the electrode is actually responding to hydroxyl radicals.

The potential set up in the dark at the film/solution interface is analogous to that at a junction between two solutions containing hydroxyl ions; the value of such a potential is given by the equation:-

$$E = (t_- - t_+) \frac{RT}{F} \ln \frac{a_2}{a_1}$$

where t_+ and t_- are respectively the transference numbers of the cations and the hydroxyl anions at the junction, and a_1 and a_2 are the mean activities of the hydroxide in the two solutions.

In this case only hydroxyl ions are moving across the boundary, so that t_+ is zero, whilst t_- is unity.

The potential at the interface is then given by the expression:-

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1}$$

On the surface of the film further from the solution, the OH^- concentration is constant, since the film is composed of iron hydroxide, and thus a_2 is constant in nature, and the above equation reduces to:-

$$\begin{aligned} E &= \text{constant} - \frac{RT}{F} \ln a_1 \\ &= \text{constant} + 0.059\ pOH \\ &= \text{constant} + 0.059(14 - pH) \\ &= \text{constant} - 0.059\ pH \end{aligned}$$

which is of the form given by the overall slope of the curve in Fig. 14.

The inflexions in the curve are probably due to permeation of the film by hydrogen ion as well as hydroxyl ion, since the greatest deviation from linearity occurs on the acid side of neutrality. The reason for the high value observed at pH 3 is not clear, though it is possible that a phase change occurs on the film material at this pH.

On irradiation of the film, the iron hydroxide is converted to a hydroxide having a valency of iron of greater than three, thus increasing the ratio of hydroxyl ion to iron on the film surface, and causing an increase in the value of a_2. This in turn gives an increase in the value of the constant in the equation, indicating a rise in potential. This theory is seen to hold below a pH of about 3.5. Above this pH there is a fall in potential which must be due either to a phase change on the electrode material or to lack of formation of higher valency state hydroxide at the higher pH's.

It is seen from Fig. 16 that, from pH 3 upwards, the addition of a fixed quantity of hydrogen peroxide produces a fall in potential which is approximately constant. This change in potential brought about by the hydrogen peroxide indicates that the perhydroxyl free radical reacts to form oxygen with the liberation of a proton and an electron.

$$H_2O_2 \dashrightarrow \cdot HO_2 + H^+ + e^-$$

$$\cdot HO_2 \dashrightarrow O + H^+ + e^-$$

The liberated electron causes the fall in potential, whilst the liberated proton is taken up by hydroxyl ion to form water. The lack of sufficient hydroxyl ion in solution below pH 4, allied with a possible phase change of the electrode material explains the large deviation at these low pH's from the values obtained for the remainder of the curve.

The initial fall in potential observed on irradiation of the electrode in ferric chloride solutions may be explained on the basis of this result in peroxide solutions, since as mentioned in the general introduction, hydrogen peroxide is almost certainly formed as an intermediate in the photo-reduction of ferric chloride solutions.

Furthermore it is seen from Fig. 17 that fast stirring of the ferric chloride solution causes a fall in potential. This would be due to peroxide being swept into contact with the electrode, since without stirring, there would be rapid decomposition of peroxide in the electrode vicinity, by catalysis on the film. That this is the probable explanation of the stirring effect is borne out by the fact that no stirring effect is observed in other solutions, or even in ferric chloride solutions on the "back" run without irradiation, where there is no peroxide in solution. On the back run the potential eventually reaches the initial value without trace of the dip observed on initial irradiation.

It would thus appear that the film consists of ferric hydroxide in an active form, which may on irradiation, via an activated complex form, be oxidised to a higher valency state. The film is also pervious to hydrogen and hydroxyl ions, being responsive to hydroxyl ion. The film is also responsive to perhydroxyl free radicals.

Redox potential and pH change.

The Pt/glass reading is of platinum electrode with respect to glass electrode; the redox of platinum electrode with respect to calomel; the pH of calomel with respect to glass electrode. So the sum of redox + pH gives redox with respect to glass electrode, i.e. Pt/glass.

Thus at time 30 minutes:-

Pt/glass = 582 m.v. redox = (766 - 241) m.v. pH = 40 m.v.
redox + pH = 565 m.v.

But this neglects the difference in asymmetry potential between the two glass electrodes used. This was measured using buffers of pH 4.00 and 7.01, and was found to be 20 m.v.

Thus:-

Pt/glass = 582 m.v.

redox + pH + asymmetry = 585 m.v.

These results are in good agreement.

In Fig. 19, due to the inertia of the galvanometer needle, the Pt/glass at 1 minute was not as high as would other wise be expected. Small changes in the Fe^{2+} concentration lead to large changes in the Fe^{3+}/Fe^{2+} ratio initially, and hence a large change in the Pt/glass. As the amount of ferrous iron becomes more appreciable, the small changes have less effect on the Fe^{3+}/Fe^{2+} ratio and so the graph becomes less steep.

This explanation also holds for the redox potential. With a complex reaction occuring, the pH would be expected to have some effect on the redox potential, whereas the straight line portion in Fig. 23 suggests that only the ferric/ferrous ratio is of importance in determining the redox potential. The equation of this line is:-

$E = 0.735 + 0.021 \log Fe^{3+}/Fe^{2+}$

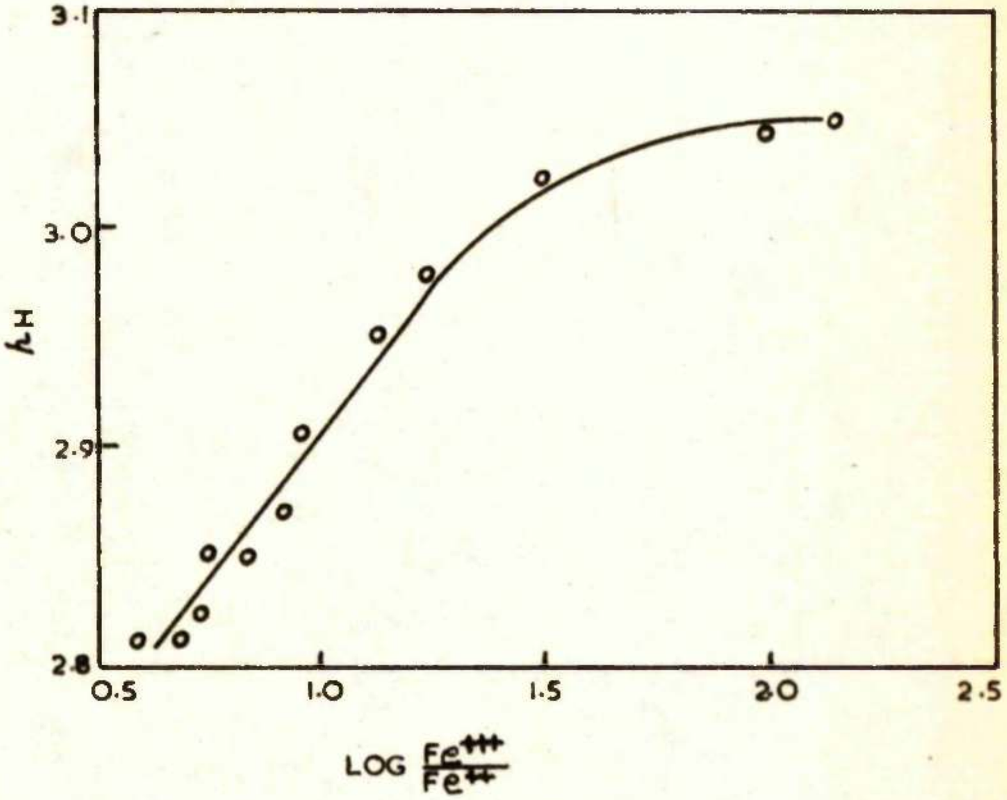
But for a ferric-ferrous system, the Standard Electrode Potential is 0.771 volts, so that the above cannot be a true ferric-ferrous equilibrium. In addition, the value of 0.021, approximately one third of 0.059, would suggest a three-electron change in the system. This, while only approximate, supports the view that the system is not a simple one.

Fig. 24 may offer an explanation. The plot of pH against log Fe^{3+}/Fe^{2+} is a straight line over a considerable section. Thus the effect of a change in the Fe^{3+}/Fe^{2+} ratio in this range will produce a linear change in the redox potential, if the pH factor is concerned in the redox equation. Where the curve of Fig. 24 deviates from linearity (towards the equilibrium potential of pH 3.05) then this effect would be expected to manifest itself in the redox potential value. It can be seen that the curve in Fig. 23 deviates from linearity in this portion.

This interference of pH could account for the apparent 3-electron change suggested above.

It would thus appear that the measurement of the potential difference between a platinum wire and a glass electrode presents a method of obtaining a continuous

FIGURE 24.



VARIATION OF pH WITH FERRIC/FERROUS RATIO record of the changes taking place in a ferric chloride solution during irradiation. The potential is reproducible, and the electrodes themselves introduce no impurities into the system.

PART 2.

The effect of carbon dioxide on dilute ferric iron solutions, and a possible photo-synthetic reaction.

INTRODUCTION.

The plant photo-synthetic reaction is notable for the storage of energy by photochemical means in the conversion of carbon dioxide to complex organic material such as carbohydrates. Formaldehyde was first suggested as an intermediate in the process by von Baeyer[79], and the fact that it has never been isolated is thought to be due to its rapid polymerisation to carbohydrates. It has long been the wish of scientists to duplicate this reaction in vitro, and it has been pointed out by Heidt et al.[80] that there is no theoretical reason to exclude the possibility of energy storing photochemical reactions produced by sunlight, which would not require a living plant.

There have been many attempts to find such a reaction. Dhar and Ram[81] report that traces of formaldehyde can be detected in rain water, particularly that falling after sunny periods, and attribute this to the reaction between carbon dioxide and water in the upper atmosphere :-

$$CO_2 + H_2O + (112,000 \text{ cals.}) \dashrightarrow H.CHO + O_2$$

which requires U.V. of wavelength 2550A. Short wave radiations passing through the ozone layer decompose water into H and OH and the hydrogen atoms may reduce CO_2

to formaldehyde. Formaldehyde decomposes at 2660A :-

$$H.CHO \rightleftharpoons CO + H_2$$

Presence of hydrogen in the upper atmosphere holds up this back reaction, and hence the formation of formaldehyde in the atmosphere and its presence in rain water.

The effect of U.V. on CO_2 was first observed by Chapman[82] who found that CO_2 decomposes in light with an increase in pressure (due to formation of CO and O_2). Berthelot[83] found that U.V. accelerates the dissociation of CO_2 and also the recombination of CO and O_2 :-

$$CO_2 \underset{\text{light}}{\overset{\text{light}}{\rightleftharpoons}} CO + \tfrac{1}{2}O_2$$

The decomposition is inhibited by excess and absence of water.

In solution, Stoklasa et al.[84] found no formaldehyde, whilst Baly et al.[85,86] found small quantities formed in this way. This was disputed by Baur et al.[87,88]. Porter and Ramsperger[89] found the yield of formaldehyde to decrease with increasing purity of the reactants.

As any reduction of the CO_2 which did take place was to very small extent, efforts were directed at finding some material which would provide a sensitised reduction process. The CO_2 solutions were illuminated in presence of different sensitizers and a search carried out for formaldehyde. The assumption that water itself acted as such had been made without any attempt to confirm this by proving the liberation of oxygen.

Bach[90] found that CO_2 and uranyl acetate reacted in light. Success in this direction was also claimed by Usher[91] and Moore[92] who obtained positive formaldehyde tests. However the material used in such reactions probably takes the part of a reductant rather than that of a true catalyst. To reduce CO_2 by uranyl or ferrous salts would be a success, since the oxidation-reduction potentials of these substances are far below the potential of the system $CO_2/H.CHO$. Still, this reduction would represent only one half of the process of photo-synthesis, the remaining half being the reduction of the oxidised catalyst (e.g. ferric iron) by water, leading to the liberation of oxygen.

Baly[93] used the basic carbonates of nickel and cobalt with incandescent lamps. The carbonates soon lost their "catalytic" capacity. This was attributed to their oxidation by oxygen produced by photosynthesis, though no direct test was produced. Difficulties arose in reproducing these first promising results.

Dhar and co-workers[94] claimed that formaldehyde could be detected after irradiation in pure solutions of CO_2 or $NaHCO_3$. The yield could be increased by the use of the following sensitizers :- $FeCl_3$, $FeSO_4$, $NiSO_4$, $CuCO_3$, $CuSO_4$, $Cu\overline{Ac}$, Cr_2O_3, $Cr(OH)_3$, $MnCl_2$, V_2O_5, $Pd(NO_3)_2$, $UO_3(NO_3)_2$, methylene blue, methyl orange and malachite green.

Baur[95] arrived at the conclusion that chlorophyll can produce formaldehyde by reduction of its two carboxyl groups at the expense of water, by the intermediary of an "auxiliary" reversible oxidation-reduction system, e.g. methylene blue. Levitt[96] states that light activated chlorophyll transfers electrons to an appropriate oxidant and removes electrons from water. The primary process of photosynthesis is thus viewed as a flow of electrons activated by light, with chlorophyll as a sort of conducting bridge between two half cells, in one of which a water molecule is oxidised by loss of two electrons :-

$$H_2O \longrightarrow 2e^- + 2H^+ + \tfrac{1}{2}O_2$$

and in the other an oxidant (intimately associated with the chlorophyll) is reduced by gaining two electrons.

Noyes[97] has put forward a kinetic theory for artificial photo-synthetic reactions. If energy is to be

.stored in a photochemical process, the initial act of absorption of a photon must be followed rapidly by additional reactions. These can be classified according to whether or not a non-absorbing species must react either with the excited absorber or with a fragment formed from its dissociation. Because of the compressed time scale in which many of these additional reactions occur, the kinetic treatment requires consideration of the special problems associated with very fast reactions. If the secondary processes produce an excited electronic or meta stable isomeric form of the original absorber, or of some other chemical species, the prospects are not good that the energy can be stored for long periods and released as desired. If the absorption of a quantum causes a dissociation into fragments, some energy can be stored by physical trapping of these fragments; however, this type of system is not promising either. The best prospect for a storage reaction probably involves a chemical reaction of the excited absorber or of a fragment from it with another chemical species. The product of this reaction must be metastable so that it can be stored until needed and can then liberate considerable energy during regeneration of the statting material.

If such a photochemical storage reaction is to be reasonably efficient, the subsequent secondary reactions must be initiated in a period of 10^{-8} sec. or less after the original absorption. This period is too short for direct experimental measurement of concentration changes, but theoretical considerations indicate that transient diffusion terms may cause the relative yields of competing reactions to differ from the values predicted by steady state kinetic equations.

As stated in the general introduction, two main processes occur on irradiation of 1.3×10^{-3}M ferric chloride solutions; these are an early onset of secondary hydrolysis and the reduction of ferric to ferrous iron.

The instantaneous or primary hydrolysis produces ferric hydroxide in solution, which eventually, with the commencement of secondary hydrolysis, produces colloidal ferric hydroxide giving the solution a characteristic reddish-brown colour.

From the work of Purdon and Milloy, it has been showm that irradiation at 20°C. of a 1.3×10^{-3} M ferric chloride solution leads to a photo-reduction of about 30%.

The competing reactions are :-

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

and $$Fe^{3+} + OH^- + OH \dashrightarrow Fe^{2+} + H_2O_2$$

Likely termination reactions taking place are :-

$$OH + Cl^- \dashrightarrow OH^- + Cl$$

and $$2Cl \dashrightarrow Cl_2$$

or $$OH + OH \dashrightarrow H_2O_2 \dashrightarrow H_2O + \tfrac{1}{2}O_2$$

Oxygen was detected during the irradiation, but chlorine was not, indicating that the photo-oxidation of water by ferric iron takes place during the course of the reaction.

In the present investigation it was decided to try the effect of carbon dioxide on the U.V./dilute iron system, it being thought possible that, in the conditions of the experiment, ferrous iron might reduce the carbon dioxide and that the subsequent ferric iron produced would be photo-reduced to ferrous, the system thus representing a true catalysis of the reduction of carbon dioxide. This would seem to be a reasonable assumption, since, as pointed out above, the oxidation-reduction potentials of the ferrous/ferric system are below those of the system $H.CHO/CO_2$.

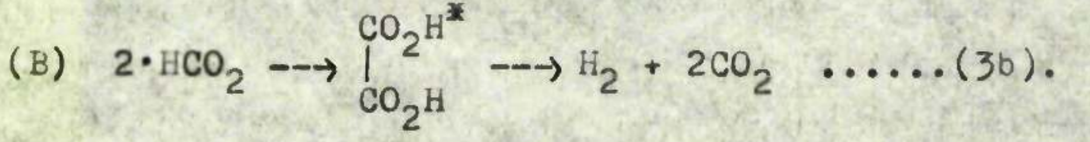
Jordan and Smith[9] mention that carbon dioxide is reduced to formic acid at the dropping mercury electrode. They have obtained evidence that $\cdot HCO_2$ is involved in this process as a transient intermediate. This is the first substantiated report of its formation in an electrode reaction though it has been produced previously by high energy radiation[98] and in a mass spectrometer[99]. They postulate the following mechanism involving alternative reaction paths :-

$$CO_2 + e^- \dashrightarrow \cdot CO_2^- \quad \ldots\ldots\ldots\ldots(1)$$

$$\cdot CO_2^- + H^+ \rightleftharpoons \cdot HCO_2 \quad \ldots\ldots\ldots\ldots(2)$$

$$\text{(A)} \qquad \cdot HCO_2 + e^- \dashrightarrow HCO_2^- \quad \ldots\ldots\ldots\ldots(3a)$$

$$HCO_2^- + H^+ \dashrightarrow HCO_2H \quad \ldots\ldots\ldots\ldots(4)$$



$$\text{(B)} \quad 2\cdot HCO_2 \dashrightarrow \begin{array}{c} CO_2H^{*} \\ | \\ CO_2H \end{array} \dashrightarrow H_2 + 2CO_2 \quad \ldots\ldots(3b).$$

The symbol * in (3b) denotes a high-energy oxalic acid species. At low concentration of carbon dioxide, reduction proceeds via path (A). At high concentrations of carbon dioxide, either path (A) or (B) may prevail. The higher the CO_2 concentration, the higher is the concentration of $\cdot HCO_2$, the faster reaction (3b) and the greater the contribution of path (B).

$\cdot HCO_2$ is an electrochemical analogue of the perhydroxyl free radical $\cdot HO_2$:-

$$O_2 \xrightarrow{e^-} \xrightarrow{H^+} \cdot HO_2 \xrightarrow{e^-} \xrightarrow{H^+} H_2O_2$$

$$CO_2 \xrightarrow{e^-} \xrightarrow{H^+} \cdot HCO_2 \xrightarrow{e^-} \xrightarrow{H^+} HCO_2H$$

Since electrode reactions represent plausible models of chemical oxidation-reduction processes, $\cdot HCO_2$ may, it is suggested, serve as a key intermediate in photosynthesis and in biological combustion processes.

Further, as was shown in the general introduction, hydrogen peroxide has been postulated as an intermediate in the ferric chloride reduction, and thus there would seem to be good reason to suppose that carbon dioxide might also take part in a reaction in ferric chloride solutions.

It was also decided to try the effect of various substrates on the system in the hope that the effect, if any could be magnified. The addition of phosphate was contemplated, since as phosphate has a complexing action on iron salts, it was thought that the photo-reduction might be slowed somewhat, in which case there would not be as great a risk of back-oxidation of the products of reduction of the carbon dioxide. In other words an attempt would be made to find a means of reducing the fierceness of the back reaction.

Salmon[98] gives evidence for the formation of soluble complexes between ferric iron and orthophosphoric acid.

(1) Orthophosphoric acid decolourises solutions of ferric chloride.
(2) The oxidation potential of the ferrous/ferric system is lowered in presence of orthophosphoric acid.
(3) The reversible oxidation of ferrous ion by iodine goes to completion in presence of orthophosphoric acid.
(4) Orthophosphates interfere in the colorimetric determination of ferric iron by thiocyanates.

The movement of iron to the anode in transference measurements on solutions of ferric salts in excess phosphoric acid is also strong evidence for the existence of anionic orthophosphato-ferrate complexes.

There are several differing views on the exact nature of the complexes formed. Various investigators report that the complexes are :-

$Fe(PO_4)_2^{3-}$ and $Fe(PO_4)_3^{6-}$ ....(100)
$FeHPO_4$ ....(101)
$FeH_2PO_4^{2}$ ....(102)
$Fe(PO_4)Cl_3^{3-}$ in presence of chloride ions ...(103)

Salmon found that iron can be removed from ferric orthophosphate solutions by using either cation exchange or anion exchange resins. Batch experiments with the orthophosphate form of an ion exchange resin indicated the presence in solution of a complex containing three orthophosphate groups per iron atom.

The pK_D for the orthophosphato-manganese complex is 2.58 as determined from acid-base titration. Presumably the ferric iron complex is even more associated, having a pK_d perhaps several units higher[104].

EXPERIMENTAL.

The preparation of 1.3×10^{-3}M ferric chloride solution has been described in part 1.

Measurement of Secondary Hydrolysis.

All the solutions investigated were initially colourless. The onset and development of secondary hydrolysis, resulting in the appearance of a gradualy deepening reddish-brown colour due to colloidal ferric hydroxide, was followed by measuring the increase in optical density with time, using a Hilger "Spekker" absorptiometer and Ilford 601 filters (peak transmission 4250A).

Analysis of Ferrous Ion.

The irradiated ferric chloride solutions were generally of the order of 10^{-4}M in ferrous ion.

For the colorimetric analysis of small concentrations of ferrous ion, the most convenient reagent is 2-2' dipyridyl used in solutions buffered to a pH in the region of 4. This reagent may be used in ferric chloride solutions only if some reagent is added to complex the ferric ion and prevent its hydrolysis, which at pH 4 is quite considerable, and interference with the analysis. Fluoride ion, complexing the ferric ion as $(FeF_6)^{3-}$ is ideal for the purpose and was found not to interfere with the red colour of the ferrous-2-2'-dipyridyl complex. 2-2' dipyridyl was therefore used in the following procedure.

2 ml. of photolysed solution were transferred to a 20 ml. graduated flask containing 2 ml. of 0.08% 2-2' dipyridyl solution, 5 ml. of buffer solution and 2 ml. of 0.25 M ammonium fluoride solution. The dipyridyl solution was prepared by dissolving 0.8 gms. in 1 litre of 0.05 N hydrochloric acid, and the buffer solution by dissolving 80 gms. of ammonium acetate together with 20 mls. of concentrated sulphuric acid in one litre of water.

The resulting solution was diluted to 20 mls. with distilled water, thoroughly shaken, and allowed to stand overnight in the dark to allow full colour development. The optical density was measured on a Hilger "Spekker" absorptiometer and Ilford 604 filters (peak transmission 5150 A).

Irradiation apparatus.

Runs on the earlier part of the investigation were carried out on the apparatus described on page 37 and shown in fig. 8, with the exception that the flask was a three-neck Quickfit of three litres capacity. The light source, unfiltered, was a 500 watt Hanovia mercury arc lamp (type S.500). Water from a constant head was arranged to flow over the outside of the flask through four jets to keep the contents of the flask at a steady 20°C. The flask was arranged on a stainless-steel table and the cooling water drained through a hollow shaft in the centre back to the thermostat tank below. The cooling water contained a little Lisapol N.D.B. detergent in order that the surface of the flask be readily wetted.

Carbon dioxide could be passed through the contents of the flask when so desired from a cylinder via a train of three potassium permanganate and one distilled water wash bottles to remove any trace of organic impurity from the gas. It was led through one of the side necks of the reaction flask.

The solution was stirred by means of a glass stirrer through the centre neck of the flask. Samples were withdrawn when required through the second side neck of the flask.

Later runs for polarographic estimation were carried out in a cell of 169 mls. capacity made from a B.40 Pyrex Quickfit socket with ground glass stopper. A short tube with an attached tap were sealed to the bottom of the cell to facilitate removal of the solution samples for analyses.

The cell was clamped over a thermostat tank from which water was pumped over the cell to maintain its temperature at 20°C. The rate of water flow was regulated by varying the voltage to the pump motor by means of a "Variac" transformer. The water drained back into the tank, splashing being prevented by allowing the small tube at the lower end of the cell to dip into the tank water. The lamp used was a G.E.C. 250 watt MED compact source mercury vapour lamp situated about 7 cm. from the cell.

Provision was made for exclusion of air from the cell during irradiation, either by passing nitrogen over the surface of the solution or by completely filling the cell with solution and inserting the stopper to exclude gas space.

The solutions were analysed for oxygen content on a Tinsley pen-recording polarograph (model MK 19). The instrument incorporates a polarising unit, an amplifier and a pen recorder.

The interpretation of polarographic steps.

There are numerous procedures for measuring the step heights of current-voltage curves, and while the final choice is quite arbitrary, it depends to some extent on the shape of the curves. Many of these procedures do not give true measurements of the magnitudes of the diffusion currents, but where a comparative method is employed for calibration, this is unimportant. The method described below illustrates the procedures adopted in the present work for determining the step height of each of the oxygen waves.

For the first wave, where the step is fairly well defined, tangents were drawn to the flattest portions at the top and bottom of the step and a further tangent at the point of greatest slope. The vertical height between the two points of intersection gave the step height. Since the second wave was not so well defined, especially at the beginning, the procedure differed in that the tangent to the bottom part was drawn parallel to the top part of the step.

A step height so measured was obtained in terms of the units into which the chart was divided. From the heights of the waves in presence and in absence of carbon dioxide, and from the fact, shown by Milloy, that oxygen evolved in ferric chloride solutions is stoicheometrically equivalent to one quarter of the ferrous ion yield, the oxygen evolution in presence of carbon dioxide was readily calculated by simple proportion.

Materials.

The water used throughout the investigation was distilled from an all glass Pyrex still. This was found to give results identical to those obtained from water distilled from alkaline permanganate.

Carbon dioxide was used from a cylinder after passing through potassium permanganate wash bottles to remove any organic impurity and then distilled water to remove any permanganate spray.

All other chemicals were of A.R. grade.

1% gelatin solution was prepared by dissolving 1 gm. of powdered gelatin in 50 ml. of water heated on a steam bath. The solution was cooled and diluted to 100 ml. with water.

pH determination.

The hydrogen ion concentration was measured with a glass electrode and a Pye pH meter.

RESULTS.

Iradiation Experiments.

A calibration curve was drawn up for the optical density of the ferrous/dipyridyl complex against the concentration of ferrous iron. A straight line graph was obtained, and from examination of the gradient, the conversion factor was obtained :-

conc. $Fe^{++} \times 10^{4}M = O.D. \times 6.65$

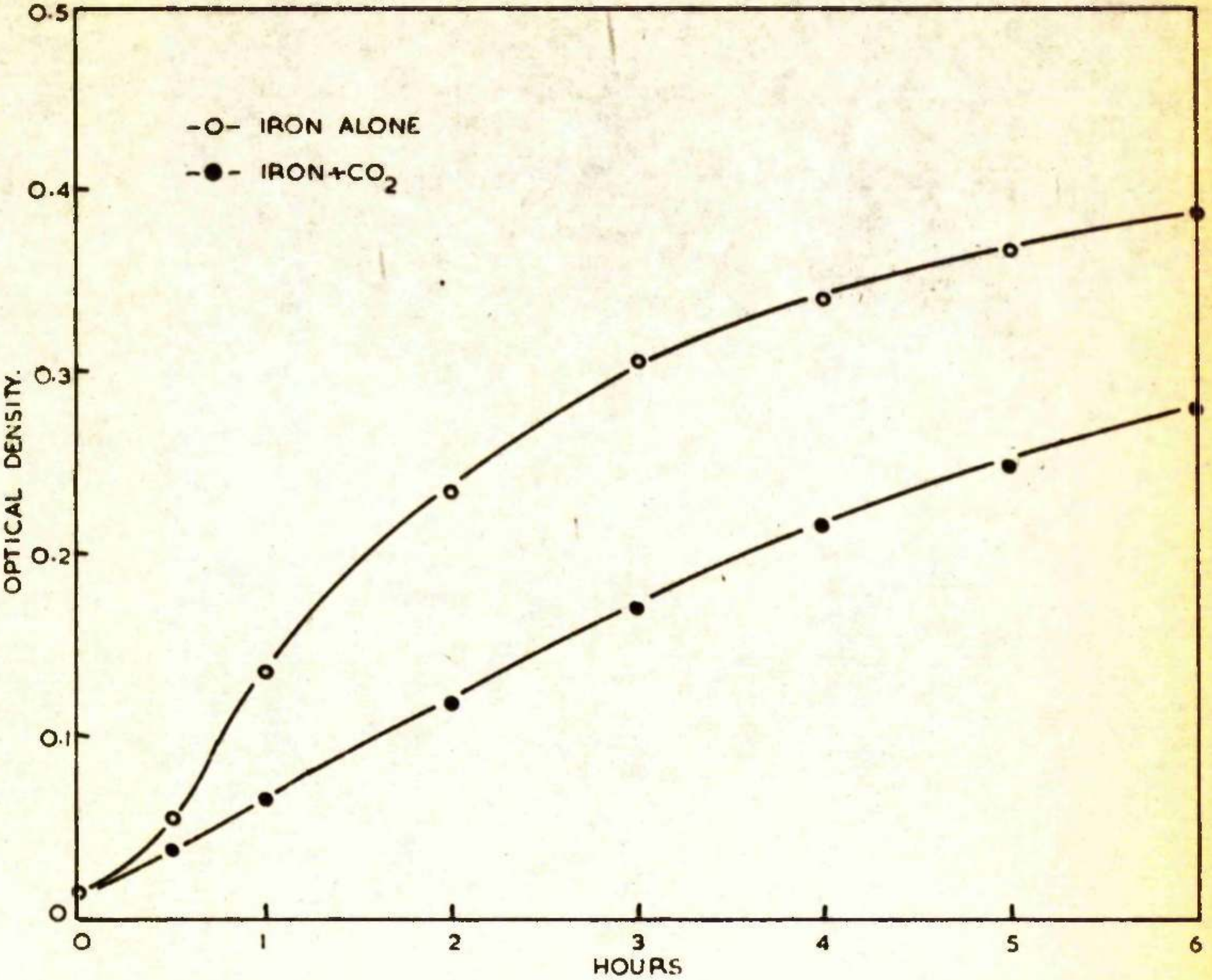
An irradiation run was carried out using two litres of ferric chloride solution ($1.3 \times 10^{-3}M$), samples being withdrawn at half hourly intervals for the measurement of secondary hydrolysis and photo-reduction. The results for theses quantities are shown respectively in figs. 25&26. It was noticed that the extent of the photo-reduction was only about one third of that reported by Purdon, a fact which may be explained on the basis that Purdon used quartz flasks, and that they were also of a smaller size than the Pyrex flask used in the present investigation. Repeat runs furnished reproducible results.

The run was repeated in presence of carbon dioxide. The gas was bubbled through the solution for half an hour before the addition of the ferric chloride melt and the commencement of the run, to allow the water to become saturated with carbon dioxide. The stirrer was operated during this period as it also was throughout the whole run. During the run the carbon dioxide was allowed to bubble slowly through the solution. The results are again shown on figs. 25&26.

It would appear that the carbon dioxide had an affect on the iron solution, since there was a substantial diminution in hydrolysis and the ferrous iron formed was reduced to approximately half that produced in absence of carbon dioxide. It was therefore decided to try to detect any formaldehyde which might have been formed dueing the course of the irradiation.

The detection technique employed was to use a modified Schiff's reagent, prepared by dissolving 1 gm. of rosaniline hydrochloride in 500 mls. of distilled water, adding 25 gms. of sodium sulphite and 15 mls. of hydrochloric acid (S.G. 1.124) and diluting to one litre. A test was run by adding 1-2 mls. of hydrochloric acid (S.G. 1.124) to 10 mls. of the test solution, followed by 1 ml. of reagent. The maximum colour was obtained after 20 hours. The solution was found to give an easily discernible colour down to concentration of formaldehyde of the order of 1 p.p.m.

FIGURE 25.



HYDROLYSIS CURVES

FIGURE 26.

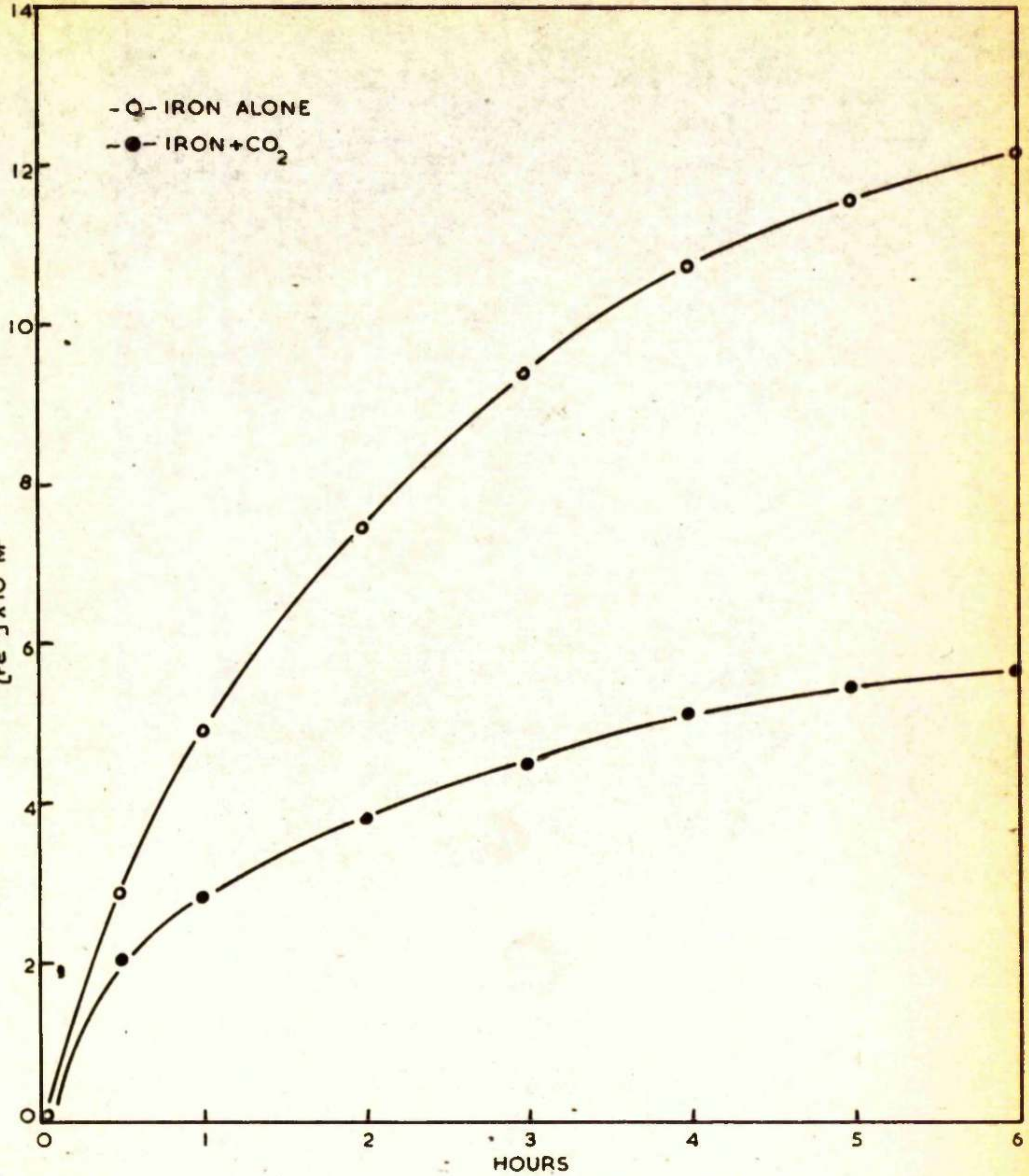


PHOTO-REDUCTION CURVES

The colour could be estimated on the Hilger "Spekker" using Ilford 604 filters.

On testing the irradiated solution both during and after completion of the run, negative results were obtained indicating the absence of formaldehyde in the solution. A run was then carried out with the addition of 10^{-4}M formaldehyde at the commencement of irradiation. Half hourly samples were withdrawn and the formaldehyde estimated colorimetrically, using the colour produced by the Schiff's reagent. It was found that after irradiation for five hours, the formaldehyde had, in the presence of iron, diminished to one third of its initial concentration.

A run, similar to the above, was carried out, using formic acid in place of formaldehyde. The method of analysis was to make the solution alkaline with potassium hydroxide to form potassium formate, add an excess of potassium permanganate, heat for 5-10 minutes on a water bath, acidify with 6N sulphuric acid, add an excess of oxalic acid and titrate the excess with preemanganate at 70°C. If T is the total volume of 0.1N $KMnO_4$, and t the volume of 0.1N oxalic acid, then :-

$$\text{wt. of formic acid} = (T - t)0.002301$$

By carrying out blank titrations on neat iron solutions and by estimating the ferrous iron colorimetrically, the titration value for the ferrous iron was obtained which was subtraced from the total titration figure to give an accurate figure for the formic acid.

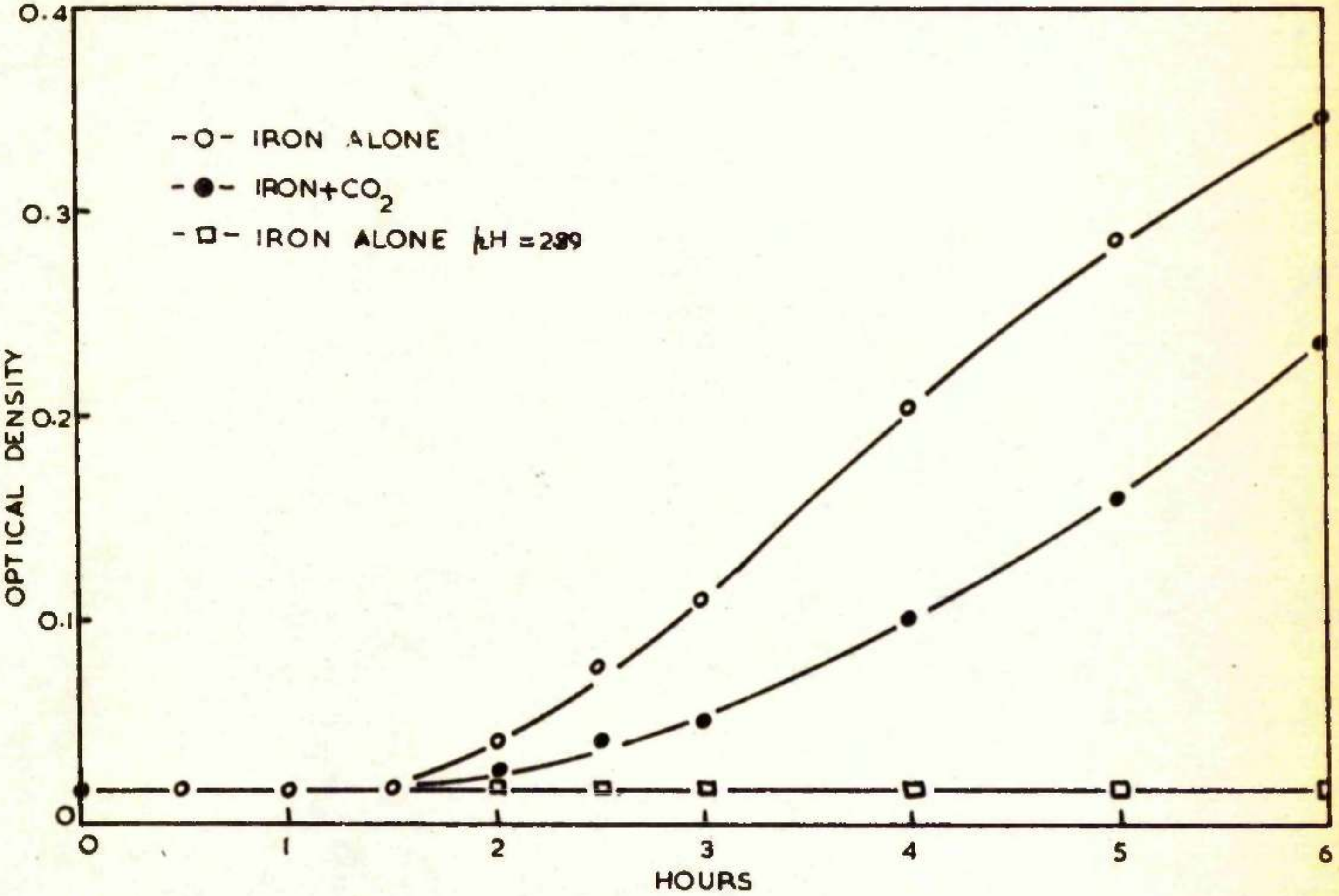
Over a five hour run, the concentration of formic acid decreased from 4.09×10^{-3}M to 2.19×10^{-3}M.

A run using oxalic acid, and analysing by direct titration against potassium permanganate solution, again correcting the titration value for ferrous ion in solution, gave a decrease in concentration over a five hour irradiation from 3.94×10^{-3}M to 1.67×10^{-3}M.

The pH of the solution was measured both in presence and absence of carbon dioxide. It was found that there was no difference large enough to account for the lowering of the photo-reduction. The iron solution had a pH of 3.05, and in presence of carbon dioxide, never fell below 2.95.

As a check on this result, dark hydrolysis curves were measured, since from the work of Purdon the effect of pH on these curves is accurately known, and also since in the dark any photochemical reaction may be precluded. The curves are shown on fig. 27, on which is also shown the dark hydrolysis curve for an iron solution of pH 2.89.

FIGURE 27.



DARK HYDROLYSIS CURVES

It is seen, that though there is a slight lowering of secondary hydrolysis, this lowering is not great enough to correspond to the lowering obtained at pH 2.89, the pH which, from Purdon's work, is necessary to give a diminution of photo-reduction such as is obtained in the presence of carbon dioxide. This is a verification of the results obtained using the pH meter.

Polarographic investigation.

Fig. 28 shows typical polarograms of 0.286 millimolar oxygen obtained with air-saturated 0.08M potassium chloride solution. The first wave results from the reduction of oxygen to hydrogen peroxide at $E_{\frac{1}{2}} = -0.13V$ vs. S.C.E.

$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$ (acid solution)

$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^-$ (neutral or alkaline solution).

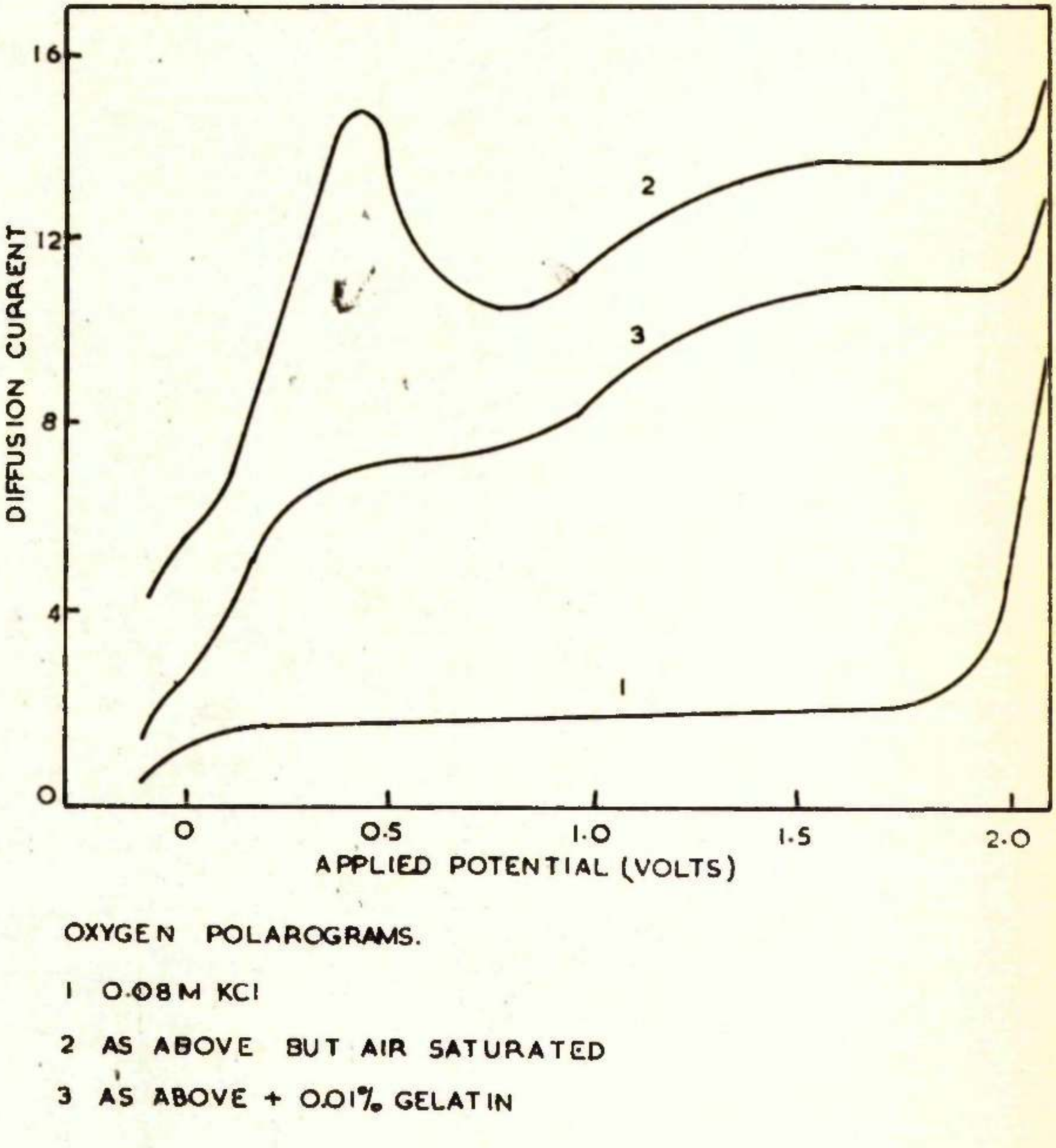
and the second wave corresponds to the reduction of the hydrogen peroxide either to water or hydroxyl ions at $E_{\frac{1}{2}} = -1.05V$ vs. S.C.E.

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ (acid solution)

$H_2O_2 + 2e^- \longrightarrow 2OH^-$ (neutral or alkaline solution)

The first oxygen wave shows a very pronounced maximum

FIGURE 28.



OXYGEN POLAROGRAMS.

1 0.08 M KCl

2 AS ABOVE BUT AIR SATURATED

3 AS ABOVE + 0.01% GELATIN

which, fortunately, is readily suppressed by surface active agents such as colloids or dye ions. The suppressor used in the present investigation was 0.01% gelatin.

Ferric iron can also give two waves, depending upon the supporting electrolyte, pH, etc., corresponding to :-

$Fe^{3+} \dashrightarrow Fe^{2+} + e^-$

$Fe^{2+} \dashrightarrow Fe + 2e^-$

which considerably complicates the oxygen determination.

The following factors had therefore to be taken into consideration when choosing a suitable supporting electrolyte and maximum suppressor for the determination of oxygen in the presence of ferric iron and photo-produced ferrous iron.

(1) It is easier to make step height measurements on the narrower first oxygen wave, especially since the hydrolysis of the ferric iron causes many solutions to have a pH sufficiently low to give a hydrogen wave which cuts short the second oxygen wave.

(2) The iron must not give waves or form complexes with the supporting electrolyte or maximum suppressor, which give waves interfering with the oxygen wave.

(3) The supporting electrolyte or maximum suppressor

must not form complexes with the ferrous iron which are readily oxidised by oxygen.

(4) The required weights of the supporting electrolyte and maximum suppressor should be easily added, preferably as small volumes of concentrated solution so that the volume ot the solution to be analysed will not be appreciably altered.

During the course of his work Milloy found no suitable supporting electrolyte which would enable the oxygen to be estimated by the narrower first wave. It appeared therefore that there was no alternative but to employ the second wave, for which potassium chloride was found to be a suitable supporting electrolyte. The 100 mls. of solution to be analysed was made 0.08M in potassium chloride by adding to it 2 mls. of an oxygen free saturated potassium chloride solution at 20°C. which is exactly 4.00M. The 0.01% gelatin was obtained by adding 1 ml. of a 1% solution.

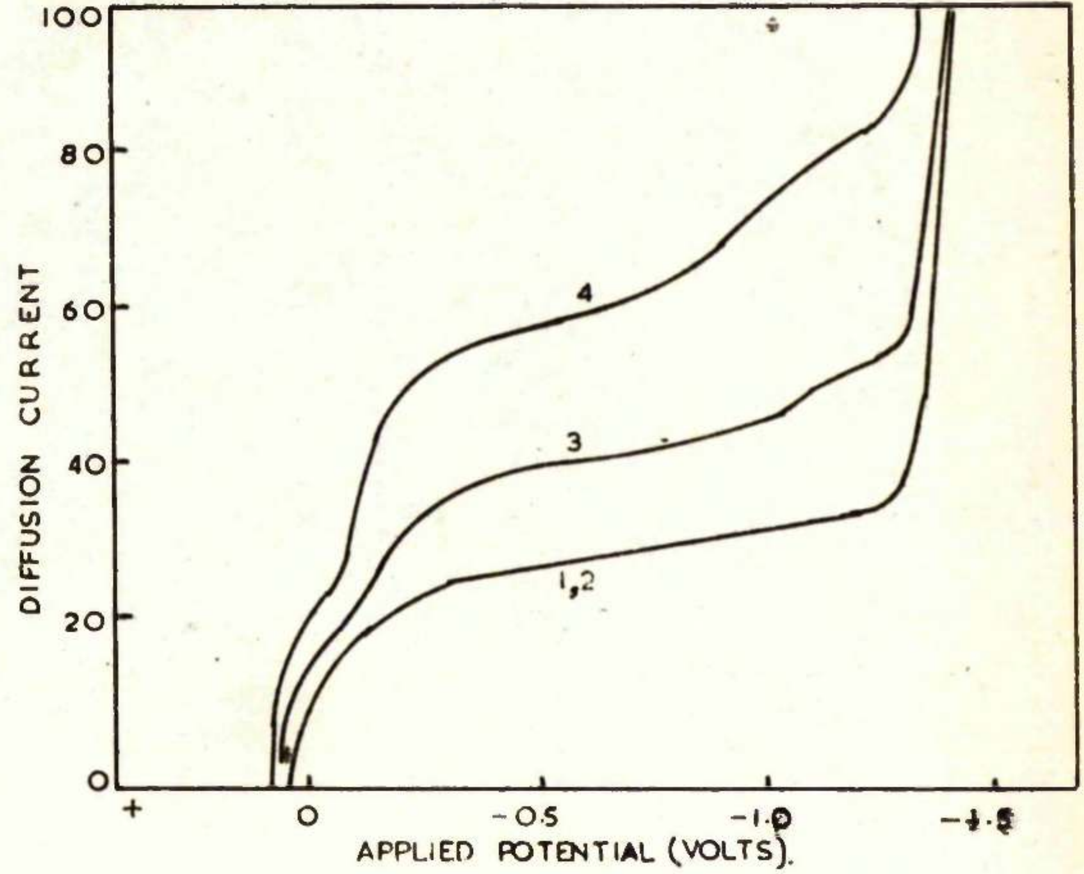
To avoid loss of oxygen from the solution during irradiation, the irradiation vessel was completely filled with solution and stoppered so as to leave no gas space above the solution. This procedure almost certainly kept the relatively small amount of photo-produced oxygen in solution, since any gas coming out of solution would have been easily seen.

A 1.3 x 10^{-3}M ferric chloride solution was irradiated for five hours and the polarogram recorded; the procedure was then repeated under exactly the same conditions except that the solution was not irradiated but kept in the dark. Finally both runs were repeated, using solution which had been made up in water which was previously saturated with carbon dioxide gas. The polarograms are shown in Fig. 29. Polarograms 1&2 are respectively for the dark and light reactions in the absence of carbon dioxide, and 3&4 for the same respective reactions in presence of carbon dioxide, all being recorded at the same sensitivity of 4.8 ua per full scale deflection.

There is no indication of a second wave at $E_{\frac{1}{2}}$ = -1.05V vs. S.C.E. in polarograms 1 & 3 showing that there was no oxygen produced in the non-irradiated solutions. It is evident therefore that the second waves in polarograms 2&4 must be due to oxygen having been produced photochemically in the irradiated solutions.

Ferrous analyses were carried out on samples of the solutions after they had been irradiated for five hours.

FIGURE 29.



OXYGEN POLAROGRAMS IN PRENCE OF $FeCl_3$

1 DARK READING IN PRESENCE OF CO_2

2 DARK READING IN ABSENCE OF CO_2

3 LIGHT READING IN PRESENCE OF CO_2

4 LIGHT READING IN ABSENCE OF CO_2

The following table gives the corresponding oxygen and ferrous iron yields, both in presence and in absence of carbon dioxide.

without CO_2 conc. Fe^{2+} = $29.8 \times 10^{-5}M$
conc. $O_2 \times 4 = 30 \times 10^{-5}M$
with CO_2 conc, Fe^{2+} = $12.1 \times 10^{-5}M$
conc. $O_2 \times 4 = 10.5 \times 10^{-5}M$

It is thus seen that, though the total yield of both oxygen and ferrous iron is reduced by the presence of carbon dioxide, the stoicheometric proportions of the two products remain unaltered.

Electrode investigation.

The apparatus used in the investigation has been fully described in part 1 of this work. (page 36).

Water saturated with carbon dioxide was placed in the cell in which was inserted a platinum electrode coated with an iron hydroxide film. By measurement the solution was found to have a pH of 3.92. The initial potential before irradiation was found to be 498 m.v. which is in agreement with the value predicted from Fig. 14.

The electrode in the solution was irradiated for thirty minutes and a rise of 122 m.v. obtained. The value predictedfrom Fig. 15 at this pH is a fall of 20 m.v. This rise in potential would be expected if the carbon dioxide was being reduced at the surface of the electrode with consequent oxidation of the electrode film material to the higher valency state form.

Because of the result just described, a further attempt was made to isolate a product from ferric chloride solutions containing carbon dioxide. In this instance the water was saturated with carbon dioxide prior to the addition of the ferric chloride melt and subsequent irradiation, and no gas was bubbled during the irradiation. After five hours of irradiation, 200 mls. of 3N sulphuric acid were added to the two litres of reaction mixture which was then transferred to a three litre Pyrex distillation unit. 20 mls. were distilled over and collected and their reaction on alkaline potassium permanganate tried. It was found that there was no decolorisation, thus showing the absence of formic and oxalic acid. Tests with modified Schiff's reagent also gave negative results for formaldehyde.

The distillation tecnique was adopted in an attempt to concentrate any possible product before the actual test, since formic acid is capable of steam distillation.

Results in Presence of Phosphate.

The initial hydrolysis and photo-reduction runs were repeated with phosphate added as substrate. Sodium phosphates were used throughout.

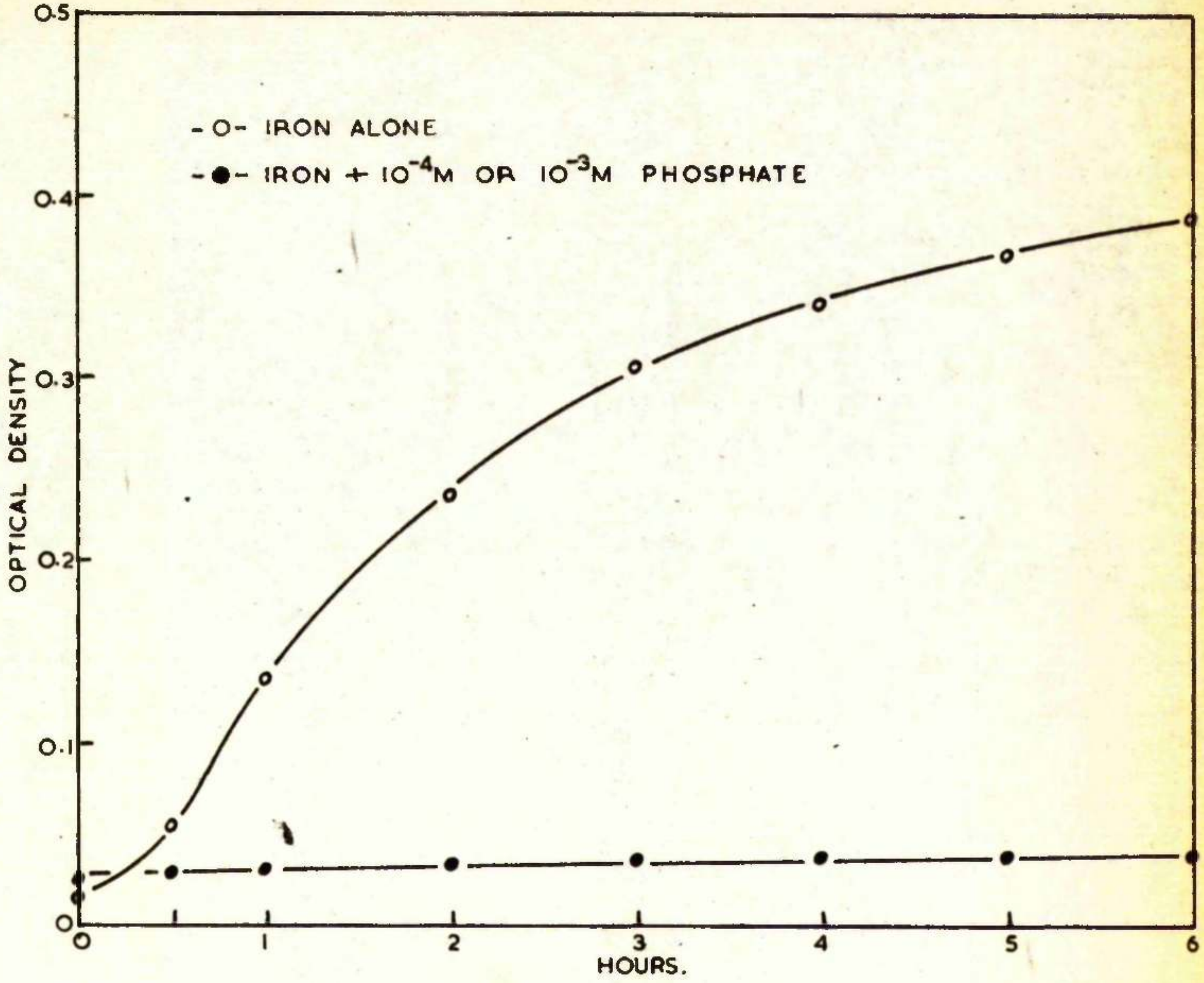
It was found that the same results were obtained irrespective of whether sodium dihydrogen phosphate or disodium hydrogen orthophosphate was used. The results for 10^{-3}M and 10^{-4}M phosphate are shown in Figs. 30 & 31 for the hydrolysis and photo-reduction respectively.

The solution containing 10^{-3}M sodium dihydrogen phosphate was a very light green colour and had a pH of 2.64. The phosphate solution alone in absence of iron had a pH of 5.04.

The solution containing 10^{-3}M disodium hydrogen orthophosphate had a greenish white colour and a pH of 2.81. The phosphate solution alone had a pH of 8.21.

A run was then carried out as above, but with the addition of 20 mls. of approximately 0.1N potassium hydroxide solution in an attempt to gain some information on the effect of the tribasic phosphate which cannot be obtained in A.R. purity. There was a white colloidal precipitate of iron phosphate when this addition was carried

FIGURE 30.



HYDROLYSIS CURVES.

FIGURE 31.

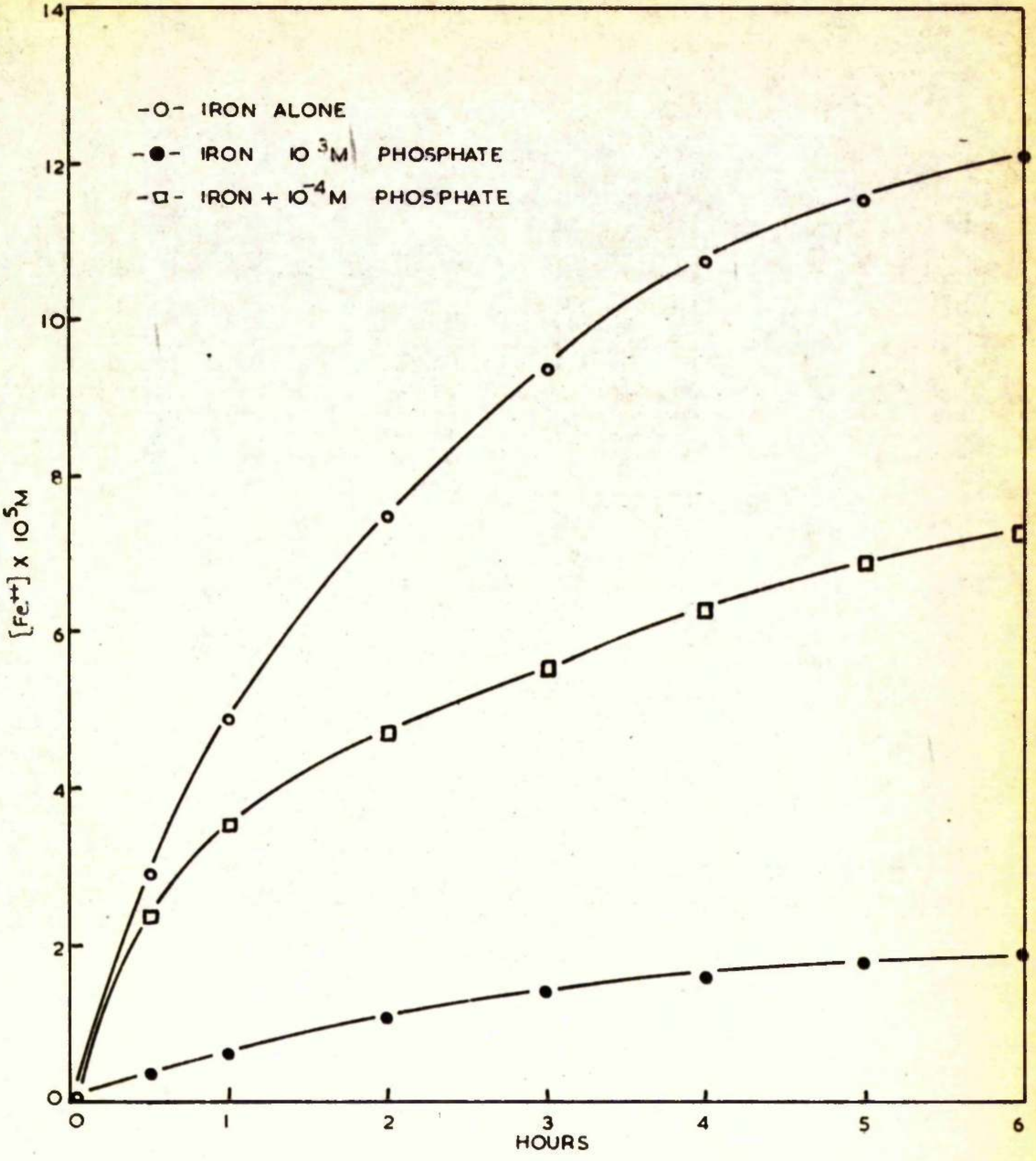
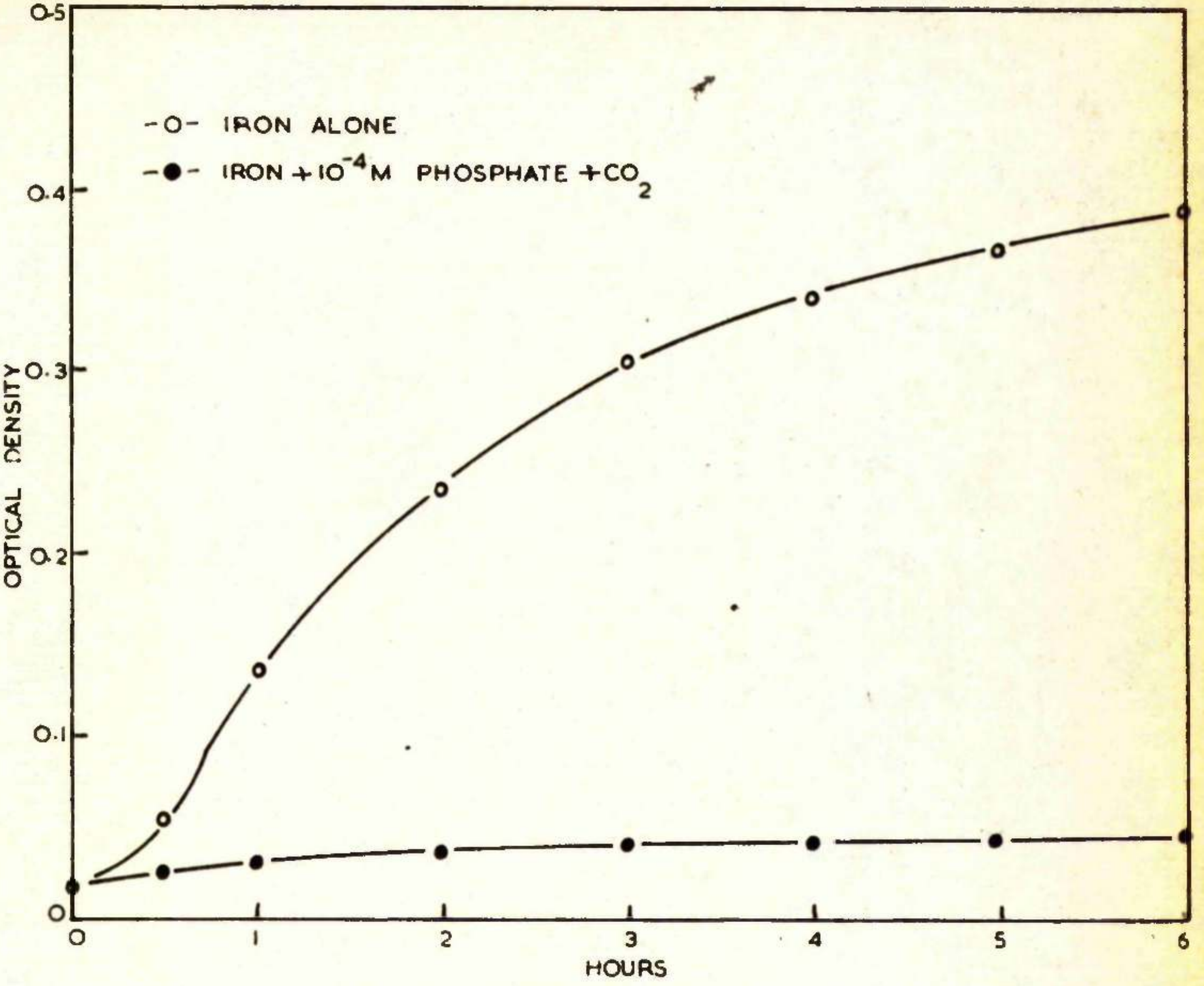


PHOTO REDUCTION CURVES

out, and it was thus considered not worth while to continue with this material.

A run with 10^{-4}M disodium orthophosphate was repeated in presence of carbon dioxide in the iron solution. Results are shown in Figs. 32 & 33 for the hydrolysis and photo-reduction respectively. It is seen that again in this case the carbon dioxide diminishes the photoreduction, though not to such a great extent as in absence of phosphate. As it had initially been hoped that the phosphate would catalyse and speed up the reaction with carbon dioxide, and this was shown not to be the case, experiments using phosphate were discontinued at this stage.

FIGURE 32.



HYDROLYSIS CURVES

FIGURE 33.

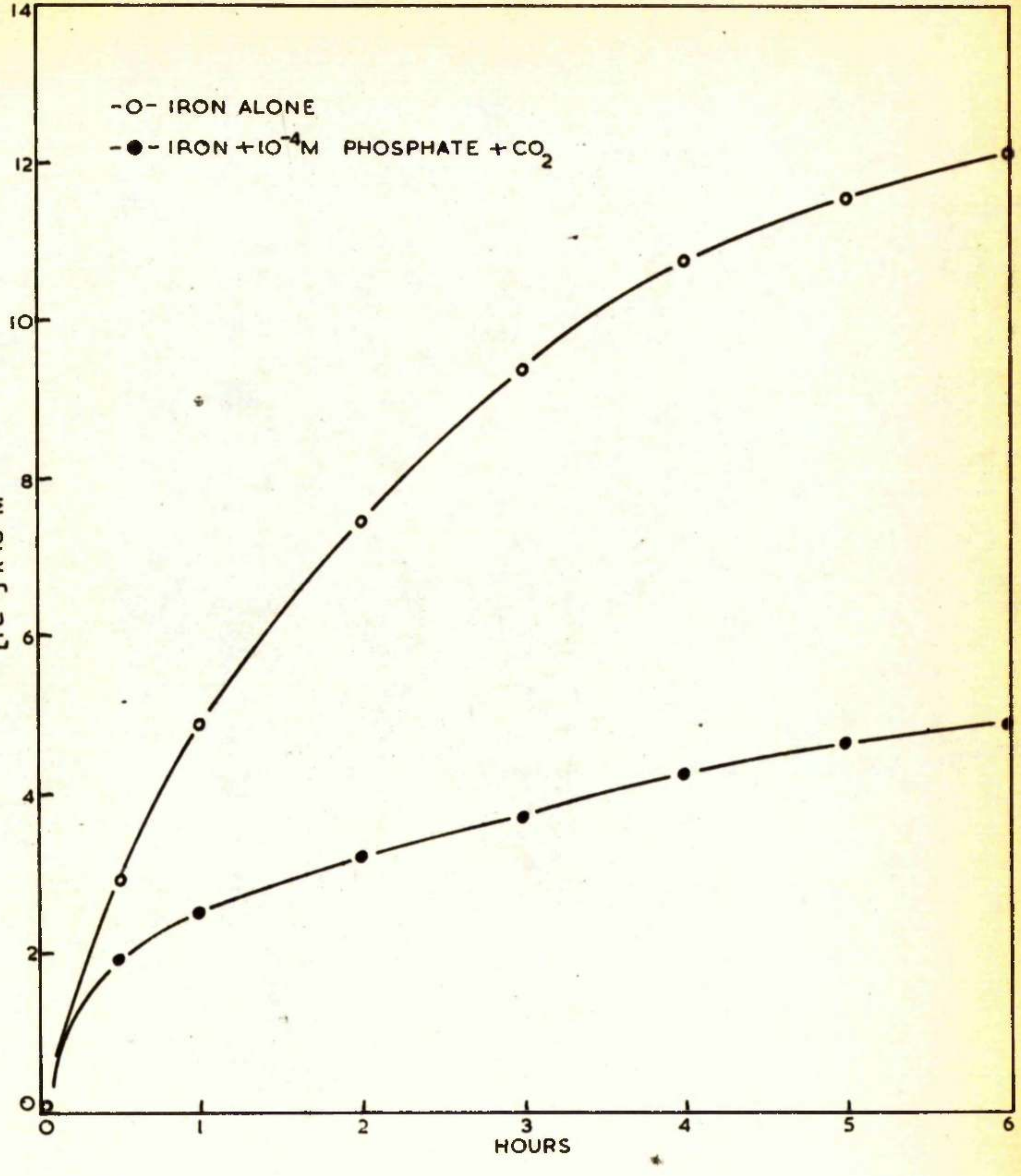


PHOTO-REDUCTION CURVES

DISCUSSION.

From Fig. 26 it is seen that the yield of ferrous iron formed after six hours irradiation was reduced from 11.9×10^{-5}M to 5.5×10^{-5}M, indicating that indeed the carbon dioxide has an effect on the normal behaviour of the ferric chloride solution. It was thought at first that this could be due merely to a diminution of pH of the solution by the carbon dioxide. However measurements on the pH meter showed that there was no lowering of large enough magnitude. As verification, the hydrolysis in the dark in presence of carbon dioxide is not entirely suppressed, though lowered (Fig. 27). This would indicate that the solutions had a pH greater than 2.89, at which there is no evidence of dark hydrolysis after six hours, whereas the photo-reduction is only lowered by approximately 5% in a solution of pH 2.89. The decrease in photoreduction in presence of carbon dioxide is, however, of the order of 50% and thus must be due to some other reaction.

The effect would be in accordance with the reaction :-

$$2FeCl_3 + H_2O \dashrightarrow 2FeCl_2 + \tfrac{1}{2}O_2 + 2HCl$$

$$CO_2 + 2FeCl_2 + 2HCl \dashrightarrow H.CHO + 2FeCl_3 + \tfrac{1}{2}O_2 \text{ ....(a)}$$

$$\text{or} \quad CO_2 + 2FeCl_2 + 2HCl \dashrightarrow H.COOH + 2FeCl_3 \text{ ....(b)}$$

where in (a) the postulated product is formaldehyde, and in (b) formic acid.

If however either of these postulations were correct, the oxygen evolved during the reaction would either be increased if formaldehyde were the product or maintained if formic acid were the product. It was however found from the experiments on oxygen determination using the polarographic method, that the oxygen yield fell in presence of carbon dioxide to an extent which was stoicheometric with the ferrous iron formed. It would thus seem at this stage that no true photo-synthetic reaction was taking place, since this would involve a reduction of carbon dioxide to some product with the consequent oxidation of water to oxygen, thus increasing the oxygen yield relative to the amount of ferrous ion produced.

The experiments using the iron oxide on platinum electrode however gave further indication of a reduction of the carbon dioxide in solution on illumination at the electrode surface, and it is a plausible supposition that, since the iron solutions contain colloidal ferric hydroxide particles due to secondary hydrolysis, a reaction of similar nature to this electrode reaction, may take place at the surface of the heterogeneous particles.

In the reaction scheme of Jordan and Smith (page 72) it will be recalled that they postulated a reaction path proceeding by alternative routes for the reduction of carbon dioxide at the dropping mercury electrode. They give the critical threshold value for the reduction to proceed via path (A) as being :- concentration of carbon dioxide less than 2.65 x 10^{-3}M.

Since in the present investigation all solutions were saturated with carbon dioxide, the concentration was above this critical value and path (B) should therefore be predominant.

Applying the scheme of Jordan and Smith to the present work, the following reaction scheme is obtained :-

$$4FeCl_3 + 2H_2O \dashrightarrow 4FeCl_2 + 4HCl + O_2 \quad \text{............(1}$$

$$2FeCl_2 + 2HCl + \tfrac{1}{4}O_2 + CO_2 \dashrightarrow \tfrac{1}{2}\left\{\begin{matrix}COOH^{*}\\COOH\end{matrix}\right. + 2FeCl_3 + \tfrac{1}{2}H_2O \quad \text{........(2}$$

$$\dashrightarrow CO_2 + \tfrac{1}{2}H_2 + 2FeCl_3 + \tfrac{1}{2}H_2O \quad \text{.....(3}$$

$$2FeCl_3 + 3/2H_2O + CO_2 \dashrightarrow 2FeCl_2 + 2HCl + \tfrac{3}{4}O_2 + \tfrac{1}{2}H_2 + CO_2 \quad \text{(4}$$

$$\dashrightarrow 2FeCl_2 + 2HCl + \tfrac{1}{2}H_2O + CO_2 + \tfrac{1}{2}O_2 \text{(5}$$

This is assuming that the reaction proceeds via path (B) and reaction (5) gives the net reaction taking place.

It is seen from these equations that the net effect would be the normal reaction of the ferric chloride solutions with an opposing back reaction which would lower the apparent rate of the forward reaction and the concentration of the products so formed.

It is further postulated that step (2) takes place at the surface of the colloidal particles, the high energy oxalic acid species then breaking down in the bulk of the solution as shown by step (3). This is in agreement with the rise in potential obtained on irradiation of the solution at the iron oxide/platinum electrode where the high energy oxalic acid species would be formed, and this would oxidise the iron oxide to the higher valency state form.

The presence of phosphate in the reaction would appear rather to damp the effect than to catalyse it. This may be explained on the basis of complex formation between the iron and the phosphate. The negligible secondary hydrolysis in presence of phosphate shows that the complex fromation, by removal of free ferric iron from solution, inhibits the formation of colloidal ferric hydroxide. The decrease in ferrous yield is similarly explained by the diminution of free iron available for reduction. The partial inhibition of the photo-reduction of carbon dioxide is probably due to the lack of colloidal particles in the solution. This also bears out the fact that the reaction is probably of a micro-heterogeneous nature, taking place at the surface of the colloidal ferric hydroxide particles.

It would appear therefore that there is a likeliehood that a photo-synthetic reaction may be catalysed by dilute colloidal solutions of ferric chloride. Unfortunately, however, the product, in this case oxalic acid, decomposes prior to its being isolated. There is perhaps a likeliehood that at very much lower carbon dioxide concentrations than those used, formic acid may be formed, but due to the small yield which would be obtained and its complexing effect with ferric iron, it is probable that a radio-labelling technique would be required before any fixation could be definitely proved.

PART 3.

The photo-oxidation of thallous salts by dilute ferric iron solutions.

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2nd April 196

Dear Dr. Mitchell

You are a member of the special committee appointed by the Faculty to examine this thesis. I shall call a meeting after I have received the External Examiner's report. Please retain the thesis meantime, and be prepared to make comments when the External Examiner's report is received.

J. M. Robertson
pp. JAB

INTRODUCTION.

Berry[105] was the first to report that the reduction of a thallic salt to the thallous condition may be effected completely by an acid solution of ferrous sulphate. The reduction proceeds quantitatively if the thallic sulphate is heated to boiling with ferrous sulphate and then cooled.

Johnson[106] investigated the rate of the reduction between 2£°C. and 45°D. in aqueous solution, 0.5 to 2.0 N in perchloric acid, and found that the rate was the same irrespective of whether thallic or ferrous ion was in excess. A forty fold increase in the initial concentration of ferric also did not alter the rate significantly. The rate increased markedly with decreasing acid concentration, suggesting that hydrolysis products of the predominant ionic species were important in the rate-determining step or steps. Bray and Hershey[107] report a value of 18×10^{-4} for the equilibrium constant for the first hydrolysis of ferric iron at an ionic strength of 1M, so that in 0.5N perchloric acid, iron (III) must exist principally as Fe^{3+}. On the basis of this evidence it seems safe to assume that Fe(II) in the same solutions exists as Fe^{2+}. Harbottle and Dodson[108] report evidence for values of from 3.2 to 6.9 for the equilibrium constant forthe first hydrolysis of thallic ion at temperatures ranging from 25°C. to 41.8°C. at an ionic strength of 6M. These values indicate that most of the Tl(III) in perchloric acid solutions less concentrated than 3M exists as $TlOH^{2+}$. By calculation they obtained $TlOH^{2+}$ to be the principal species in 0.5 to 2.0N perchloric acid, and proposed as mechanism for the reduction :-

$$Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^+$$

$$Fe^{2+} + TlOH^{2+} \dashrightarrow FeOH^{2+} + Tl(II)$$

$$Fe^{2+} + Tl(II) \dashrightarrow Fe^{3+} + Tl^+$$

$$Tl(II) + Tl(II) \dashrightarrow Tl^{3+} + Tl^+$$

or a small fraction of the reactants, probably $TlOH^{2+}$ is further hydrolysed and either one or two electrons are passed from Fe^{2+} to the hydrolysed product, TlO^+ :-

$$TlOH^{2+} \rightleftharpoons TlO^+ + H^+$$

$$Fe^{2+} + TlO^+ \dashrightarrow FeO^+ + Tl(II)$$

$$FeO^+ + 2H^+ \dashrightarrow Fe^{3+} + H_2O$$

Forcheimer and Epple[109] proclaimed that the specific rate decreased slightly in presence of oxygen. The products do not affect the rate and chloride ion acts as an inhibitor. Where the concentrations of Tl(III) and chloride ion are equivalent, the Tl^{3+} is capable of complexing all the chloride present. The rates observed when chloride less than equivalent to the Tl(III) concentration are present, approximated to the second order rate expected if the Tl(III) concentration was replaced by the quantity (Tl(III) - Cl^-). However the rate was somewhat faster than calculated using this "reduced concentration" and the chloro-complexes must account for a fraction of the reaction.

At acid concentrations between 0.75 and 1.5 N the rate of reaction decreases with increasing acid concentration illustrating the important part which hydrolysed species play in the reaction as shown by Johnson. Between 2.6 and 4.0 N the rate of the reaction increases with increasing acid concentration, due, perhaps, to a kinetic salt effect, or perhaps the perchlorate ion concentration itself has a positive effect on the reaction due to ion pair formation. Attempts were made to study the reaction at lower acid concentration, but the hydrolysis of Tl(III) solutions interfered (thallic hydroxide precipitates only slowly from solutions when the solubility product is not greatly exceeded. The solubility product of $Tl(OH)_3$ was found to be 8.8×10^{-44} by letting a small excess of $Tl(OH)_3$ precipitate from a 0.5 N perchloric acid solution. Th s value is in good agreement with the value of 1.5×10^{-44} calculated by Sherrill and Hass[110].

The kinetics put forward were :-

$$Tl(III) + Fe(II) \dashrightarrow Tl(II) + Fe(III)$$

$$Tl(II) + Fe(II) \dashrightarrow Tl(I) + Fe(III)$$

or alternatively :-

$$H_2O + Tl(III) + Fe(II) \dashrightarrow FeO^{2+} + Tl(I) + 2H^+$$

$$FeO^{2+} + Fe(II) + 2H^+ \dashrightarrow 2Fe(III) + H_2O$$

No choice can be made between iron(IV) and thallium(II) as an intermediate. However the path through Tl(II) is to be preferred since an intermediate which can act as a reducing agent is necessary to explain the induced oxidation by oxygen[109].

Contrary to previous work, Ashurst and Higginson[111] showed that iron(III) retarded the rate. This is consistent with the mechanism :-

$$Tl(III) + Fe(II) \rightleftharpoons Tl(II) + Fe(III) \text{ ....(1)}$$

$$Tl(II) + Fe(II) \rightleftharpoons Tl(I) + Fe(III) \text{ .....(2)}$$

Johnson had attributed the fall-off of second order rate plots after 60% reaction to analytical error, whilst

Forcheimer and Epple ascribed the effect to atmospheric oxygen. Both were unable to distinguish between the two most probable reaction schemes: in (1) the initial oxidation-reduction step is the 1-electron transfer reaction :-

$$\mathrm{Tl(III) + Fe(II) \longrightarrow Tl(II) + Fe(III)}$$

followed by :-

$$\mathrm{Tl(II) + Fe(II) \longrightarrow Tl(I) + Fe(III)}$$

in (2) the 2-electron transfer reaction :-

$$\mathrm{Tl(III) + Fe(II) \longrightarrow Tl(I) + Fe(IV)}$$

is the first step, followed by :-

$$\mathrm{Fe(IV) + Fe(II) \longrightarrow 2Fe(III)}$$

Air has no significant effect on the reaction.

The reaction velocity constant, obtained from the initial gradient of the simple first or second order plot, decreases as the initial concentration od Fe(III) is increased and the curvature of these plots becomes more pronounced. Increases in the initial concentration of Tl(I) have no effect. The retarding effect of Fe(III) is ascribed to the reversal of reaction (1). With regard to Johnson's conclusions about the nature of the reacting species, the form of the variations of the rate with hydrogen ion concentration indicates only that the reaction between Tl(III) and Fe(II) can take two paths involving the formation of two transition complexes, the one including Tl^{3+}, Fe^{2+} and OH^- and the other including Tl^{3+}, Fe^{2+} and $2OH^-$. Thus, for example reaction between Tl^{3+} and $FeOH^+$ cannot be distinguished from that between $TlOH^{2+}$ and Fe^{2+} and it is incorrect therefore to identify the constants with teactions between specific ions.

More work was done on the reaction at high chloride concentration by Duke and Bornong[112] who found that a minimum in the rate of reaction occurred at Cl^- concentrations between 0.1 and 12M. At higher concentrations of Cl^-, the rate increased steeply and levelled off between 1.5 and 2.0M. The conclusion was drawn that Tl(II) must complex Cl^-. (Fe^{2+} = 0.095M, Tl^{3+} = 0.05M, H^+ = 2.50M).

An investigation by Hu and Scott[113] to determine whether or not thallous complexes exist in chloride solutions showed that in aqueous solution of KCl, NaCl and NH_4Cl containing excess TlCl, the only complex ion present in appreciable concentration is $TlCl_2^-$, except in KCl solutions of high concentration.

Biedermann[114] studied the hydrolysis equilibrium of

Tl(III) solutions and found that only mononuclear ions, $Tl(OH)^{2+}$ and $Tl(OH)_2^{+}$ were formed. This is in agreement with the result obtained by Hietanen and Sillen[115].

The reduction of thallic ions in acid solutions by alpha and gamma rays was studied by Lefort and Tarrago[116] who also investigated the effect of the concentration of thallous ions on the reaction. They found reduction yields of 3.10 and 2.36 respectively for alpha and gamma radiation. The very slow reaction of hydrogen peroxide with thallic ions was stated to be catalysed by the rays. Tl^{2+} ions are intermediate products; their formation promotes a chain reaction of reduction by H_2O_2.

$$OH + Tl^{+} \dashrightarrow Tl^{2+} + OH^{-}$$

competes with :-

$$OH + OH \dashrightarrow H_2O_2$$

in the vicinity of the ray paths where free radical concentration is high. Thus Tl^{+} concentration influences the radiation yield.

Bednar[117] found that the reverse reaction took place when Fe(III) sulphate and Tl(I) sulphate were irradiated by X-rays in presence of 2-2' dipyridyl. There was a large increase in the normal reduction of the iron, particularly at small H_2SO_4 concentrations. This was explained by the reactions :-

$$Tl^{+} + OH \dashrightarrow Tl^{2+} + OH^{-}$$

$$Tl^{2+} + Fe^{3+} \dashrightarrow Tl^{3+} + Fe^{2+}$$

It was evident that other reactions were taking place which reduced the amount of reduction. The velocity of these reactions is similarly dependent on the H_2SO_4 concentration. This phenomenon however cannot be explained definitely from the results though it is not impossible that e.g. the reaction :-

$$OH + H_2SO_4 \dashrightarrow H\ O + HSO_4$$

plays a definite part.

In a further paper, Bednar[118] studies the reduction of ferric salts by X-ray radiation in presence of 2-2' dipyridyl in absence of thallous ion. The effect of oxygen and the concentration of H_2SO_4 and of Br^- on the reduction was investigated. Competitive reactions occur between H atoms and Fe^{3+} ions and O, and between OH radicals and I^- and Br^- ions. At higher pH, the Fe^{3+} ions are also reduced by peroxidic radicals from the 2-2' dipyridyl.

In the iron system at present under investigation, light causes a reduction of Fe(III) to Fe(II) and simultaneous oxidation of water to oxygen. It was therefore decided to carry out an investigation as to the effect of Tl(I) on the reaction to see whether the iron solutions were strongly enough oxidising to cause an apparent reversal of the reaction predicted from the electrochemical potentials of the ions taking part, and in an attempt to postulate whether the reaction intermediate was Tl(II) or Fe(IV).

EXPERIMENTAL.

Materials.

Water. The water used was purified as described in Part 1 (page 43).

Ferric chloride. The A.R. salt was used and the solutions were made up from the melt by using an "Agla" micrometer syringe as described in Part 1 (page 44).

Ferric nitrate. The A.R. salt being unobtainable for this compound, a new unopened bottle with no smell of nitric fumes was used. Since the material is very hygroscopic, making the accurate weighing of small quantities rather difficult, it was decided to use a method similar to that employed in making up the ferric chloride solutions. It was found, however, that the salt remained in the supercooled condition for rather a short time, and that when it solidified, it had a large coefficient of expansion and cracked the containing tube. A small quantity of water was added, just sufficient to maintain the liquid state on cooling. A suitable quantity was found to be 5 mls. to 30 mls. of ferric nitrate melt. From calculation, verified by titration against titanous chloride solution, it was found that to give a solution of 1.3×10^{-3}M required 0.3602 mls./litre of solution.

Thallous salts. These were B.D.H. salts of the best available purity.

Thallic oxide. This material was made by adding 100 vol. hydrogen peroxide to a solution of a thallous salt containing excess pure alkali hydroxide. The brown precipitate was filtered and thoroughly washed to remove all trace of alkali and peroxide. The product was then dried in the oven at 100°C.

Apparatus.

The apparatus used during the investigation consisted of a three litre Pyrex flask with three quickfit necks. Stirring was achieved by having a stirrer inserted in the centre neck. The contents of the flask were maintained at a steady 20°C. by spraying the surface of the flask from four water jets fed from a large thermostat tank below the apparatus, the jets being fed from a constant head to which the water was pumped from the bath below.

The light source was an unfiltered Hanovia S.500 mercury vapour lamp.

Analysis.

Hydrolysis. To follow the hydrolysis of the iron solutions, the optical density of the solution was measured on a Hilger "Spekker" using Ilford 601 filters. 4 cm. cells were used.

Ferrous iron. This was estimated colorimetrically using the complex formed with 2-2' dipyridyl, as described in the previous section of this work (page 41.).

Thallium. A method of analysis was required which differentiated between thallous and thallic concentration, and since any of the chemical methods which could easily be employed were inapplicable in the presence of iron, a method was devised for carrying out the analysis polarographically.

Two waves are shown on the polarogram[119]. The first coincides and merges with the anodic solution waves of mercury (0.0 V vs. S.C.E.) and is attributed to Tl(III)/Tl(I) reduction. The second wave occurs at $E_{\frac{1}{2}} = 0.463 \pm 0.003$ V vs. S.C.E. and is due to Tl(III)/Tl(0) reduction. Tl(I) polarograms are also formed and the Tl(I)/Tl(0) wave occurs at $E_{\frac{1}{2}} = -0.462$ V vs. S.C.E. Solutions containing Tl(III) and Tl(I) can be analysed by measuring the current at -0.26 V ($i_{III/II}$) and at -0.70 V (i_{tot}) and then applying the equation :-

$$i_{I/0} = i_{tot} - 1.51 \times i_{III/I}$$

which comes from :-

$i_{III/O} = 1.51 \times i_{III/I}$ where 1.51 is an experimentally determined constant.

In practice the above method was found to be unsatisfactory, since iron interfered with the Tl(III)/Tl(I) reduction wave. However, since the total concentration of thallium in the solution was always known, the following method was used for estimating the ratio of thallous to thallic present :-

$i_{III/I} = 3.82$

$i_{III/O} = 5.72$

$i_{I/O} = 2.65$

where i is the diffusion current in the Ilkovic equation, and the actual values are obtained from paper 119 above.

Thus :-

$i_{III/O} - i_{III/I} = 5.72 - 3.83 = 1.89$

At zero time in the run, there is only Tl(I) present and the step height by measurement is 66.5 units (from an actual determination using a solution of 10^{-3}M thallous solution).

Assuming 100% conversion to Tl(III) :-

From the above data, the step height would then be :-

$\frac{66.5 \times 1.89}{2.65} = 47.4$ units.

This is in excellent agreement with the value of 47.5 units obtained from an actual run using a solution of 10^{-3}M thallic oxide dissolved in dilute hydrochloric acid.

Thus the decrease in step height for 100% conversion during a run is 19.1 units, and from this value, the conversion during a run of Tl(I) to Tl(III) may easily be calculated by measuring the decrease in step height of the polarogram of the solution as the run proceeds.

The polarograms were run on solutions containing 0.1M KCl, since in this medium, voltages obtained against the mercury anode pool correspond to those obtained against the S.C.E. and thus obviate the necessity of using a calomel electrode. In the present investigation, the half-wave potential is not of vital importance in any case, since only one wave occurs in the region under investigation and the step height is the unknown quantity which it is required to measure. The solutions also contained 0.001% gelatin to suppress maxima.

The polarograph used was, as before, a Tinsley automatic pen-recording instrument.

Zero time on all runs was taken as the time of switching on the lamp.

RESULTS.

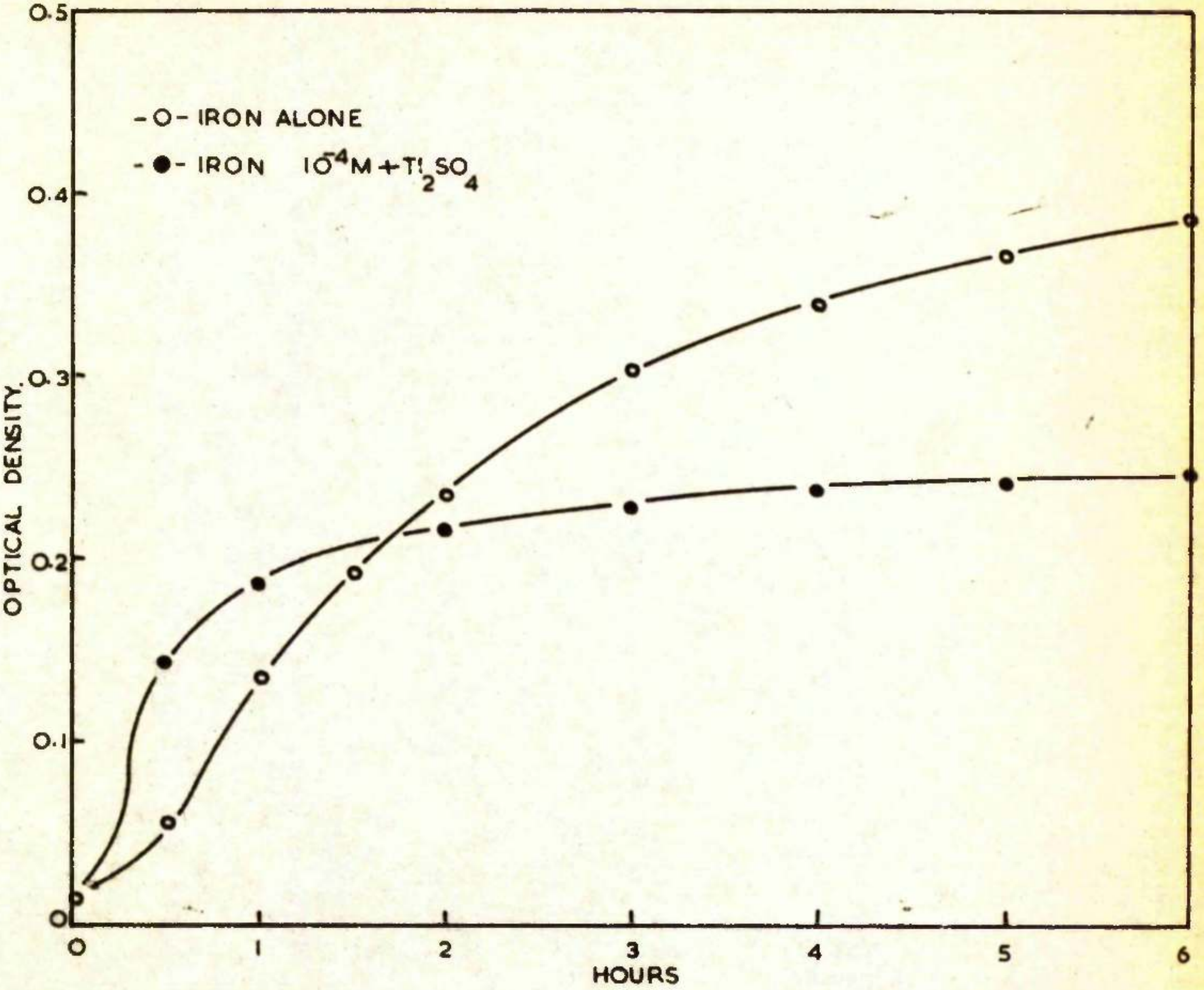
Six-hour irradiation runs were carried out using thallous sulphate as substrate in 1.3 x 10^{-3}M ferric chloride solutions, at concentrations of thallous sulphate of both 10^{-4}M and 10^{-3}M. The hydrolysis curves are shown in Fig. 34 and those for the photo-reduction of the iron in Fig. 35, which graphs also contain the results for neat iron solutions with no substrate for comparison. It will be seen that in the hydrolysis curves, no results are shown for 10^{-3}M substrate. This is due to the fact that at this concentration there is a brown precipitate of thallic hydroxide in the solution, and no accurate results could be obtained for the hydrolysis.

The above runs were repeated using thallous chloride as the substrate. The results are shown in Figs. 36 & 37.

A run was next carried out, again using thallous chloride as substrate, but in an iron solution which had been aged for twenty four hours in the dark at 20°C prior to addition of the substrate and subsequent irradiation. The results for hydrolysis and photo-reduction are shown respectively in Figs. 38 & 39.

Since Purdon[32] reported that the addition of the substrate glucose caused a rapid increase in the rate of

FIGURE 34.



HYDROLYSIS CURVES.

FIGURE 35.

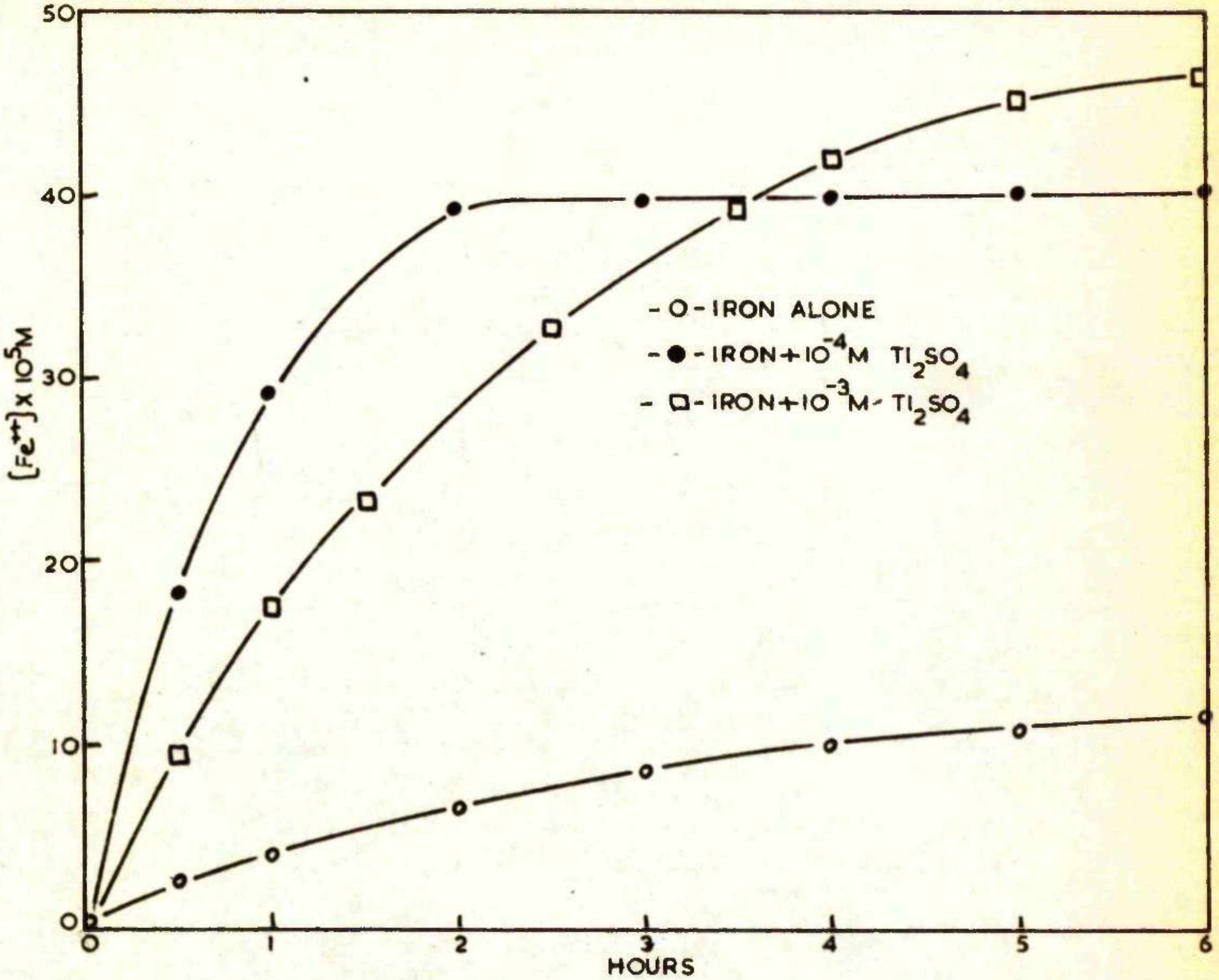
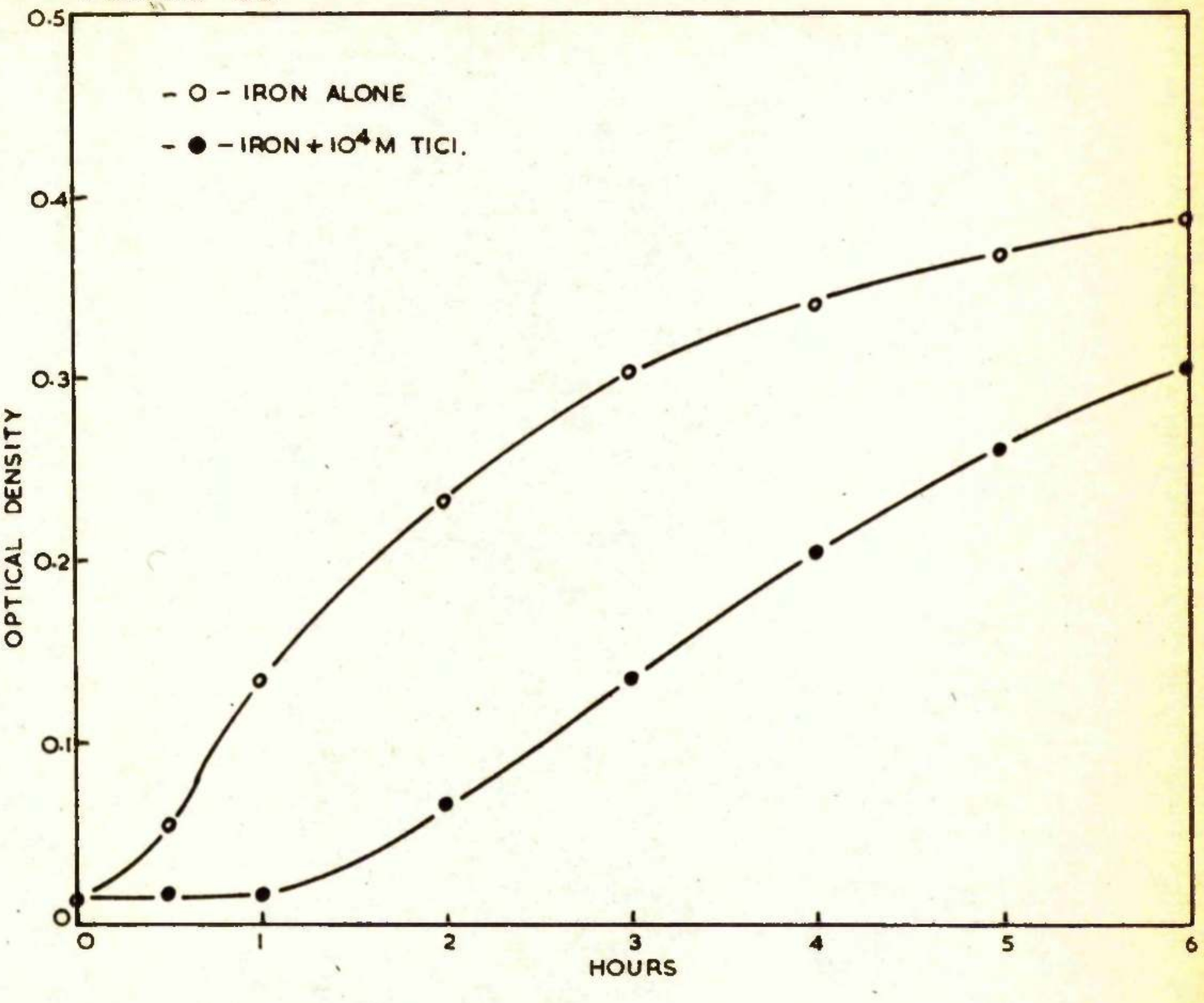


PHOTO-REDUCTION CURVES

FIGURE 36.



HYDROLYSIS CURVES.

FIGURE 37.

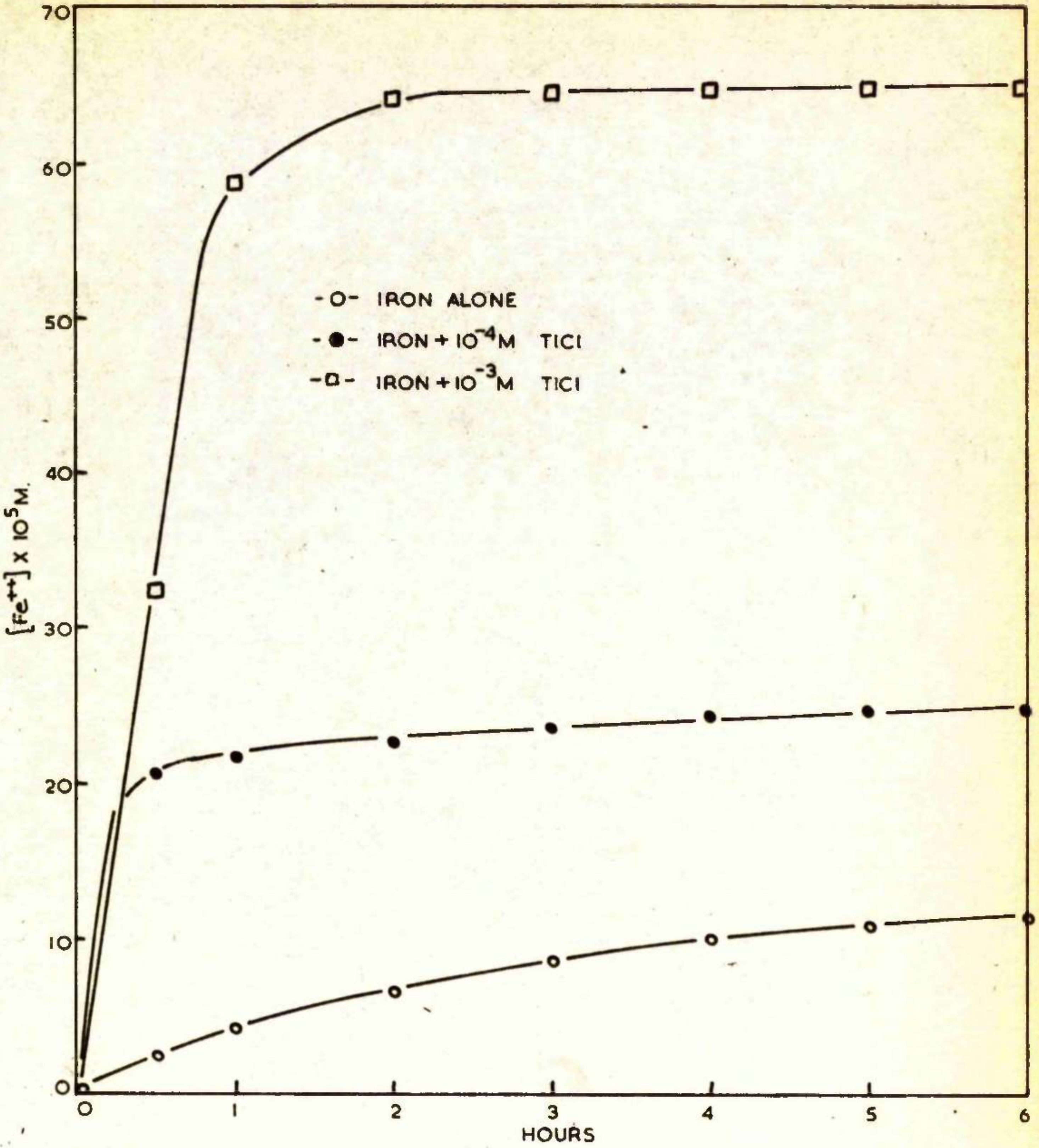
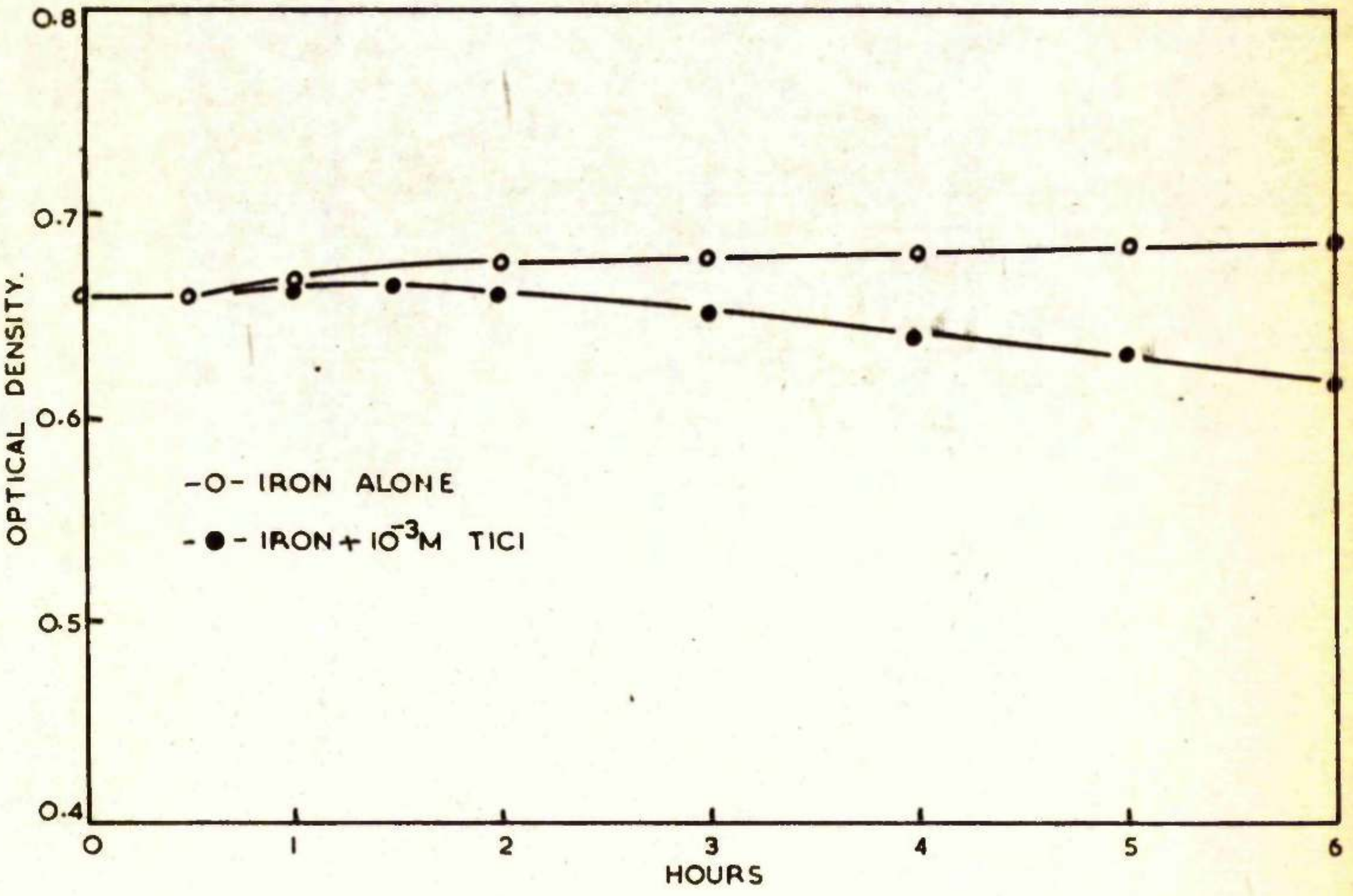


PHOTO REDUCTION CURVES.

FIGURE 38.



HYDROLYSIS CURVES OF SOLUTIONS AGED 24 HOURS BEFORE IRRADIATION.

FIGURE 39.

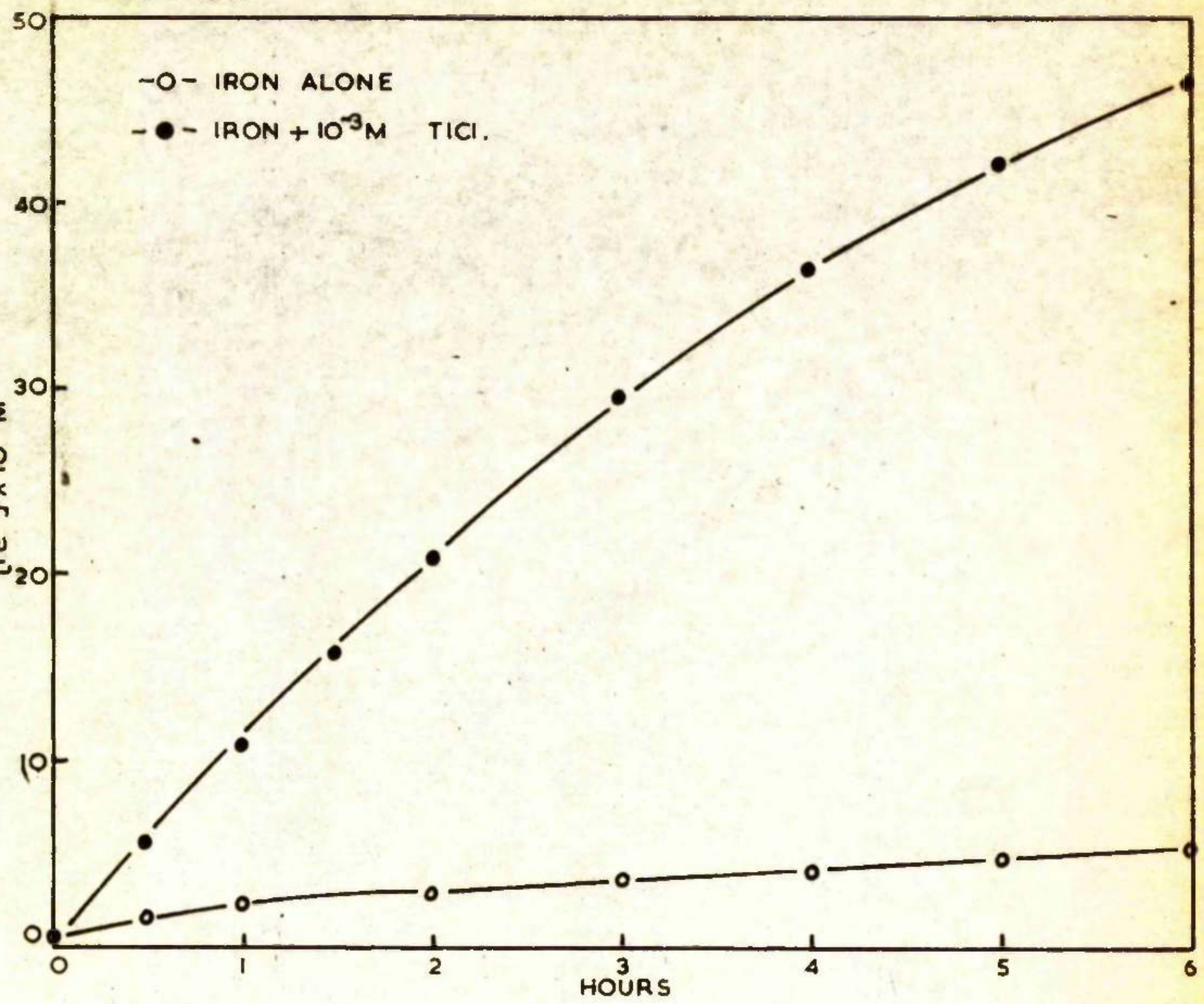


PHOTO REDUCTION CURVES OF SOLUTIONS AGED 24 HOURS BEFORE IRRADIATION.

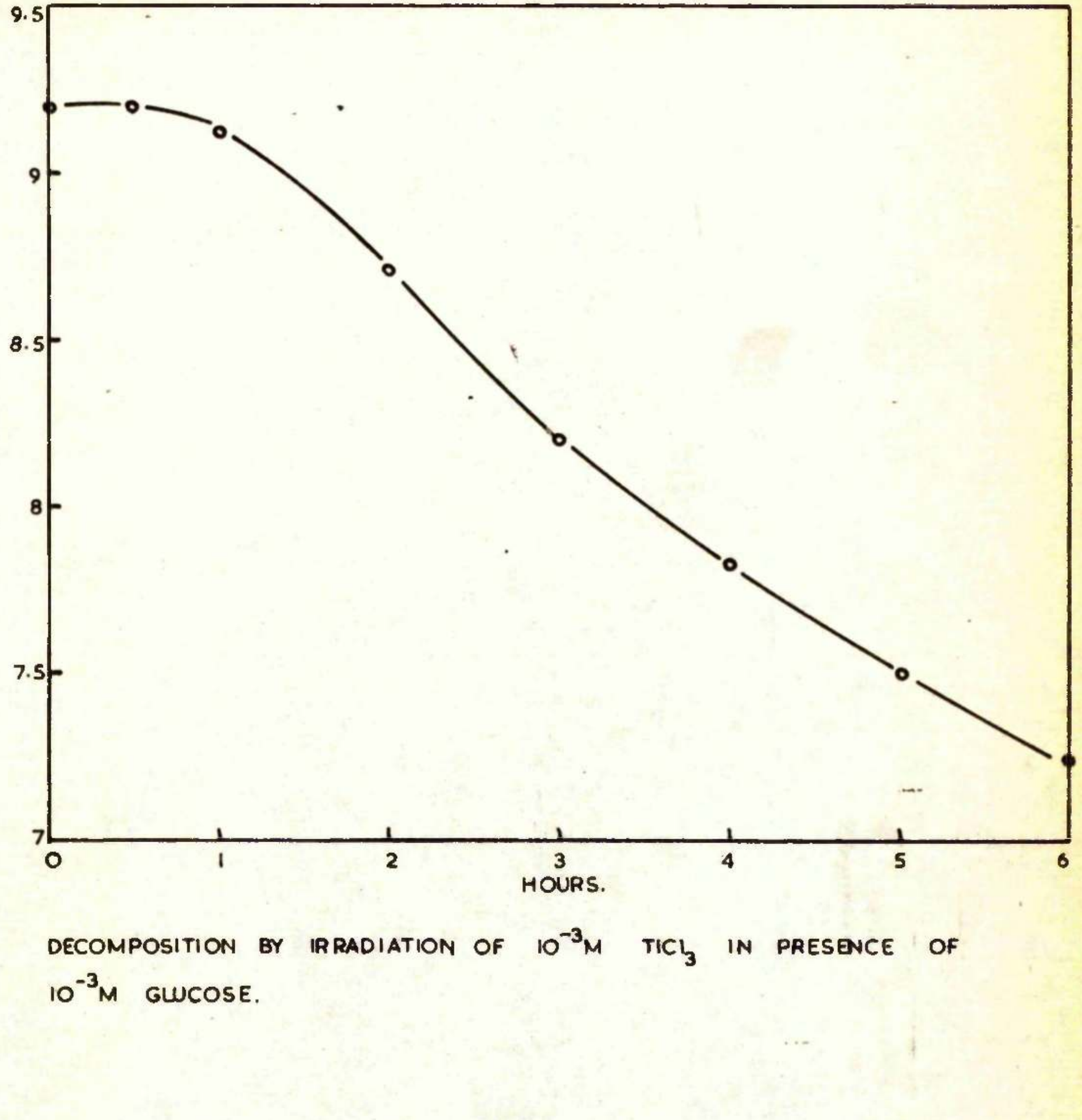
photo-reduction of ferric iron solutions, it was decided to try the effect of glucose on a solution of thallic chloride under irradiation. 10^{-3}M glucose was irradiated in presence of 10^{-3}M thallic chloride and the solutions analysed at hourly intervals for thallic ion. The analysis was carried out colorimetrically by withdrawal of 20 ml. samples to which were added 2 mls. of 1% glucose solution and 0.5 mls. of 1N NaOH solution. The resulting solution was analysed on the "Spekker", using Ilford 601 filters. The results are shown in Fig. 40.

Since it was felt that sulphate and chloride might have a complexing effect on the reaction, a run was next carried out using 10^{-3}M thallous nitrate as substrate in 1.3 x 10^{-3}M ferric nitrate solution. The results for hydrolysis and photo-reduction of the iron solution are shown respectively in Figs. 41 &42.

Polarograms were run at various intervals on the solutions in the above runs to ascertain whether the iron reduction was stoicheometric with the thallium oxidation, or whether the thallous salts were acting as catalysts in the photo-reduction of the ferric iron.

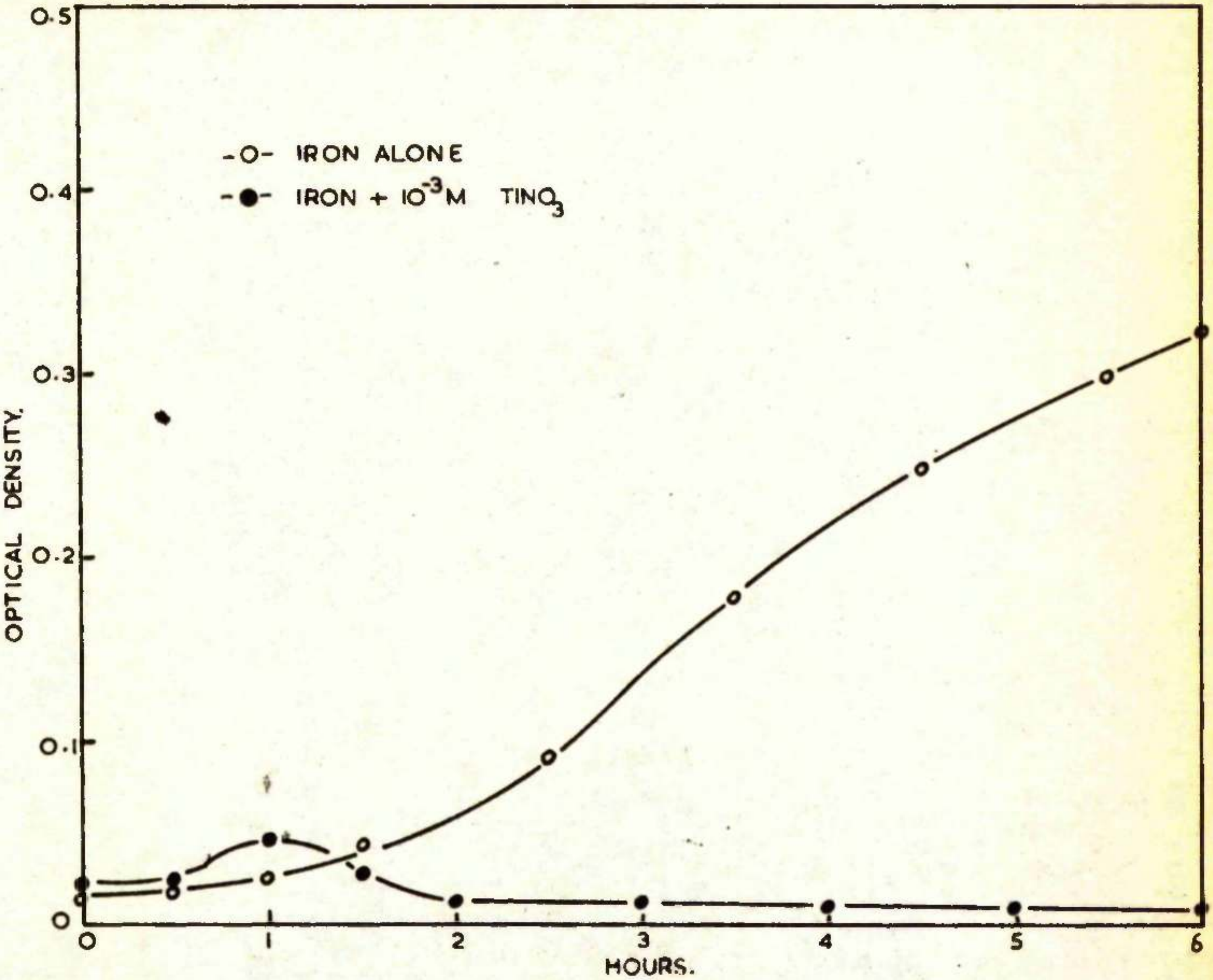
A sample result at 10^{-3}M thallous chloride from which

FIGURE 40.



DECOMPOSITION BY IRRADIATION OF 10^{-3}M $TiCl_3$ IN PRESENCE OF 10^{-3}M GLUCOSE.

FIGURE 41.



HYDROLYSIS CURVES OF FERRIC NITRATE.

FIGURE 42.

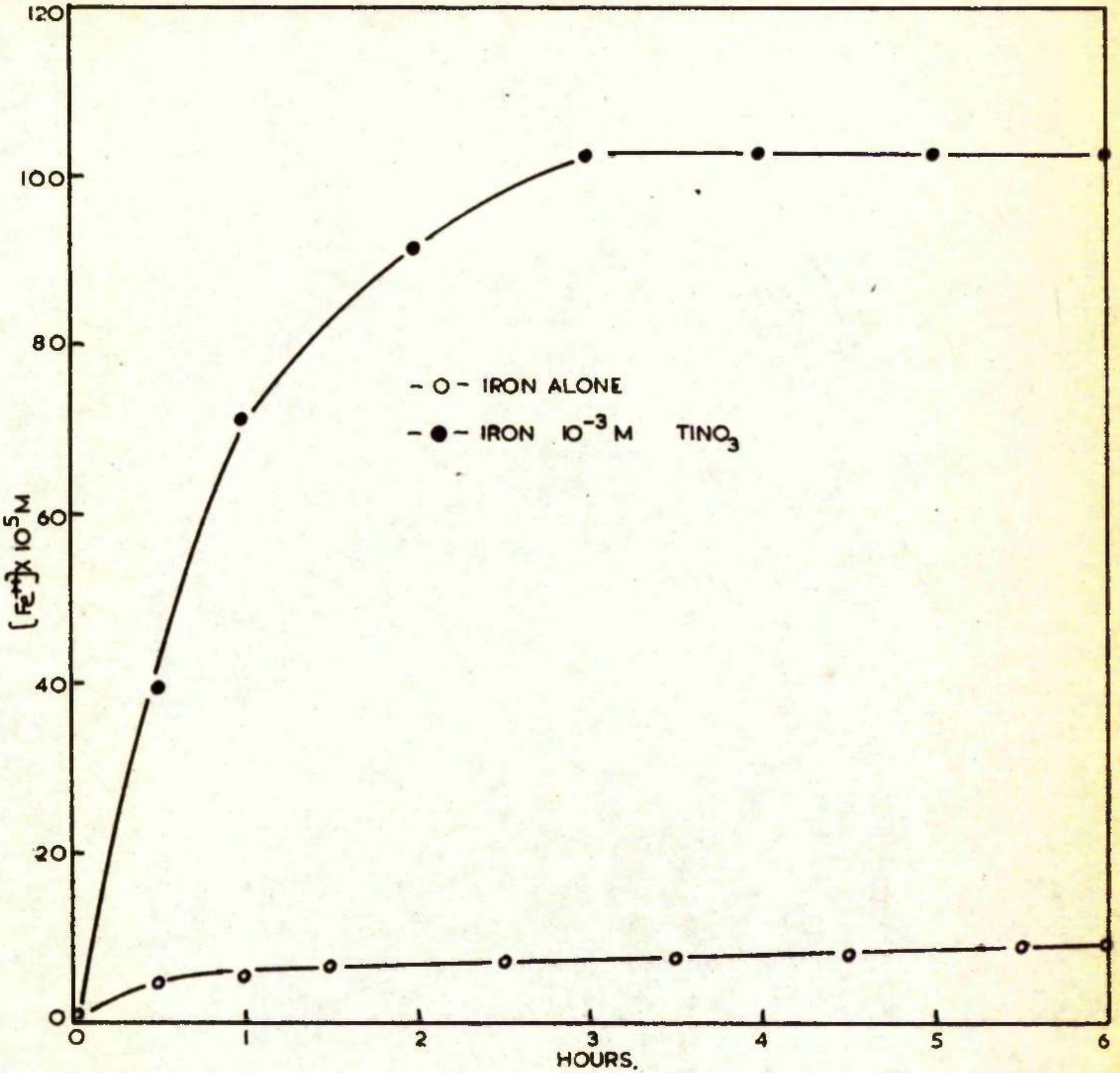


PHOTO-REDUCTION CURVES OF FERRIC NITRATE.

the results for Fig. 37 are taken is shown below.

As shown in the experimental part of this section, for 100% conversion, the decrease in step height is 19.1 units.

Time	Step ht. dec.	Tl^{+} dec. x 10^{3}M	Fe^{2+} inc. x 10^{3}M.
0	0	0	0
½	3	15.6	32.4
1	5	26.0	58.8
2	6	31.5	64.2
3	6	31.5	64.3
4	6	31.5	64.4
5	6	31.5	64.5
6	6	31.5	64.5

It is seen that alowing for the one valency change in the case of the iron and the two valency change in the case of the thallium, the results show stoicheometry in accordance with the overall reaction :-

$$2Fe^{3+} + Tl^{+} \xrightarrow{h\nu} 2Fe^{2+} + Tl^{3+}$$

Results for other runs gave corresponding stoicheometry throughout.

Thallium solutions were next investigated in the photo-voltaic apparatus described in Part 1 of this work.

Thallic oxide was dissolved in hydrochloric acid to give a solution of thallic chloride at pH 2. A rise of 14 m.v. was obtained on irradiation of the iron oxide film on platinum electrode through the thallic solution. On irradiation of the electrode through a solution containing 10^{-3}M thallous chloride at pH 2, a rise of 47 m.v. was obtained. On switching off the lamp and leaving the system for two hours, it was found that in the case of the thallic solution, the potential had fallen to the original value, whereas in the case of the thallous solution, the potential had fallen to 43 m.v. below the initial value before irradiation. It will be recalled that at this pH, irradiation of the electrode in hydrochloric acid causes an increase in potential of 195 m.v.

DISCUSSION.

In Fig. 34 it is seen that an initial boost given to the hydrolysis in the presence of thallous sulphate quickly falls off after about two hours. It is not clearly established whether indeed the initial apparent boost is due to an increase in the actual hydrolysis or whether the solution becomes optically denser due to the formation of a ferric sulphate complex in colloidal form. This is quite likely, since at the higher concentration of thallous sulphate, a distinct precipitate forms. The eventual lowered extent of hydrolysis is common to all substrates so far added to the system amd may be partially explained by the increased photo-reduction which causes a consequent diminution in the quantity of ferric ion available for hydrolysis.

The overall equation for the reaction may be represented as :-

$$Tl_2SO_4 + 4FeCl_3 \xrightarrow{h\nu} 2TlCl_3 + 3FeCl_2 + (FeSO_4)_{complex}.$$

This reaction is in agreement with the stoicheometry obtained from the polarographic analyses. Since this is in the opposite sense to the normal reaction for these ions, and since there is no reverse reaction on removal of the irradiation, it may be postulated that a chloro-thallic complex is causing the reaction to proceed to the right.

For all of the thallous ion to react, each mole of Tl^+ requires three moles of Cl^-, all of which must come from reaction with the iron in solution. Thus at 10^{-4}M Tl^+, 3×10^{-4}M Cl^- is required, and the iron reacting must therefore be 3×10^{-4}M. To this figure is added the 10×10^{-5}M from the reaction in the absence of substrate, and the final figure of 40×10^{-5} is obtained, which is seen to be in good agreement with that obtained experimentally as shown by the photo-reduction curve in Fig. 35.

At the higher concentration of thallous ion, the good agreement no longer holds, since the whole reaction is held back due to the formation of appreciable quantities of sulphate complexes in the system.

Similar results are obtained using thallous chloride, the reaction is this case being :-

$$TlCl + 2FeCl_3 \xrightarrow{h\nu} TlCl_3 + 2FeCl_2$$

In this case the thallous chloride can itself supply one mole of Cl^- and only two moles are required from the iron to take up all the thallium in a chloro-complex. Thus, 10^{-4}M Tl^+ requires 2×10^{-4}M iron to react. To this is added the normal 10 x 10^{-5}M and a total of 30 x 10^{-5}M iron reacting is obtained, which is in agreement with the figure for the photo-produced ferrous ion in Fig. 37.

At 10^{-3}M it is seen that the iron reacting is very much greater than in the case of the sulphate, though yet not as high as would be expected on the basis of the above argument. This is probably again due to complex formation in the system, though this does not occur to the same extent in the chloride medium as in the sulphate medium. This is borne out by the hydrolysis curves, where there is no initial boost in this case, due to colloidal particles of complexed iron, but there is still a visible precipitate at the higher concentration.

When thallous nitrate is added to a solution of ferric nitrate as shown in Fig. 42, it is seen that on irradiation there is a rapid photo-reduction of the iron, to an extent which stoicheometrically corresponds to the conversion of thallous to thallic ion. In this case, however, the reaction reverses on switching off the light and overnight the ferrous present in solution diminished by 25%. It is also seen that the rise in the ferrous concentration is not so rapid as in the runs carried out in the presence of the chloride ion, indicating that though the reaction will take place in the absence of chloride, the latter prevents the back reaction from taking place.

In the nitrate solutions, the hydrolysis is seen to decrease after an initial rise. This is due to the fact that the oxidation of the thallium is strong enough to bring the iron out of the hydrolysed state and reduce the ferric iron to the ferrous state. To confirm this, runs were carried out on iron solutions which had been aged for 24 hours in the dark before the addition of the substrate and subsequent irradiation. The results as shown in Figs. 38 & 39 show that again the reaction is strong enough to bring the iron out of the "hydrolysed" condition and reduce it to the ferrous state.

The exact stoicheometry of the iron with the thallium in the nitrate solutions, with the absence of the additional "normal" concentration of ferrous formed of 10×10^{-5}M is also explained on this basis, since the normal reaction is not of sufficient strength to bring any further iron out of the hydrolysed state to become available for reduction to ferrous ion.

As shown in Fig. 40, glucose is a strong enough reductant to cause reduction of the thallic chloride in solution, though ferrous iron is not.

From the experiments with the photo-voltaic apparatus, it may be concluded that the normal high rise in potential on irradiation is inhibited by complex formation in the film, due to the thallic ion present in solution. When thallous ion is present in solution, there is a larger rise in potential than that obtained in the presence of thallic. The rise in potential is thought to be due to an increase in the valency state of the iron oxide forming the film on the electrode. This reaction is caused by the action of light on the film material. The quadrivalent iron formed in this transition can then oxidise thallous iron in solution at the surface of the electrode when the lamp is switched off and since the potential falls during this period to a value approximately of the same magnitude as was the rise on illumination, it is supposed that there is a two valency change with respect to the iron which is reduced to the ferrous state on the film.

This is in accordance with the mechanism :-

$$Fe(OH)_3 + H^+ \xrightarrow{h\nu} FeO^{2+} + e^-$$

followed by :-

$$FeO^{2+} + Tl^+ + H_2O \longrightarrow Tl^{3+} + Fe(OH)_2$$

It is also suggested that since electrode reactions represent plausible models of chemical oxidation-reduction processes, that the reaction of thallous and ferric salts on irradiation in solution takes place through this iron(IV) stage, rather than through a thallium(II) stage.

It would therefore appear that the reversal of the normal iron/thallium reaction which has been observed in this work is due firstly to the action of light on the system, probably causing the formation of iron(IV) on the surface of the colloidal ferric hydroxide particles, and acting as an intermediate in the reaction, and secondly to the formation of strong chloro-thallic complexes, retaining the thallium in the trivalent state after its photochemical formation in the system.

PART 4.

The decomposition of hydrogen peroxide by dilute ferric iron solutions, and the micro-heterogeneity of the system.

INTRODUCTION.

Purdon showed quite beyond doubt that colloidal ferric hydroxide plays a major part in the photo-reduction of dilute ferric chloride solutions. There are a number of possible explanations as to the mechanism of the increased photo-activity shown on hydrolysis. They are described below.

The formation of hydrogen peroxide is suggested as an intermediate in the photo-oxidation of water by ferric iron. In the analogous ceric system , the decomposition of the peroxide to oxygen by ceric ion is not considered to be rate determining. However, in the iron system, the hydrogen peroxide formed will back oxidise some of the photo-produced ferrous ion leading to a decreased yield of ferrous iron. Thus the rate at which the peroxide decomposes will play a large part in the determination of the final Fe^{2+} yield. The increased photo-activity on hydrolysis might therefore be due to a large increase in the rate of decomposition of the peroxide to oxygen by ferric ion. It was decided to study the effect of the extent of hydrolysis of the iron on the rate of peroxide decomposition.

A heterogeneous effect in the photo-oxidation of water, when the vessels were packed with silica, was reported by Dain and Kachen[120]. Increased oxygen evolution was observed and it is suggested that the surface catalyses the recombination of OH radicals.

$$OH + OH \longrightarrow H_2O + \tfrac{1}{2}O_2$$

A similar effect might be expected with iron solutions and an investigation into this was thus carried out.

The mechanism of the iron catalysed decomposition of hydrogen peroxide has been fully discussed in the general introduction to this work.

Barb et al.[49] have found that the decomposition is first order with respect to hydrogen peroxide concentration in ferric nitrate solutions, at temperatures from 25° to 45°C. at pH's 2.3 and lower, in which the H_2O_2/Fe^{3+} ratio is greater than unity. When this ratio is reduced to between unity and 0.002, the decomposition becomes 1.5 order and by varying the hydrogen peroxide concentration these authors found that the change in order is a function not of the amount of reaction, but of the peroxide concentration. This is in agreement with the results of Andersen[53] who observed that with lower H_2O_2/Fe^{3+} ratios, the reaction appears to have order higher than first. In both of these investigations, acid was added to the solutions to suppress the hydrolysis of the ferric ion.

The present investigation is chiefly concerned with the decomposition of hydrogen peroxide solutions at pH 3.05 and temperature 20°C. catalysed by 1.3×10^{-3}M ferric chloride solution in which hydrolysis takes place during the reaction.

Some work has also been carried out on the decomposition in iron solutions which have had the ferric hydroxide particles removed by filtration through a "Millipore" filter disc.

EXPERIMENTAL.

Materials.

Water. The water used was distilled from an all-glass Pyrex still and was found to give results identical to those obtained from water triple distilled from alkaline permanganate.

Ferric chloride. A.R. hydrated ferric chloride was used, and the solutions were prepared by adding the melt to distilled water as described in part 1 of this work.

Hydrogen peroxide. The hydrogen peroxide used was prepared by dilution of 86% w/v (obtained from Laporte Ltd.) unstabilised solution with distilled water, and storing in a standard flsk , in which decomposition of the peroxide was only very slight.

Silica gel. B.D.H. silica gel was used. It was given ten washings with distilled water, and by measurement was found to have no effect on the pH of the iron solutions. After five washings, the wash waters had a constant pH equal to that of the distilled water used for washing, and the silica gel was taken as being pure.

All other materials were of A.R. grade.

Apparatus and Reaction Technique.

Silica gel. 0.5 gms. were added to the reaction flask at the commencement of a run and the hydrolysis and photo-reduction measured on the "Spekker" as described in detail in part 1 of this work. Particular care was taken in the reading of the initial blank values to be subtracted from subsequent readings, since the suspension of silica gel in the solution raised the optical density of the solution by a considerable amount. The apparatus used was that described on page 77.

Hydrogen peroxide. The majority of peroxide determinations were carried out without irradiation. The reaction solutions were prepared in a 500 ml. blackened flask, the peroxide being added to the iron solution, and zero time being taken as the instant of peroxide addition. Samples were withdrawn by pipette at three minute intervals for titration, a standard procedure of withdrawal being adopted, i.e. commencement of discharge of pipette at exact three minute intervals. The samples were put into titration flasks containing 5 mls. of 3N sulphuric acid to inhibit further reaction before the actual titrations were carried out. The peroxide was determined by direct titration against N/50 potassium permanganate solution.

The cupric salts added were prepared by dilution from stock solutions made from the A.R. salt. Copper sulphate was used in the majority of the runs, though since this might have caused a complexing effect, the nitrate and chloride were also tried, but it was found that the results obtained were identical with that given by the sulphate.

Filtration of the hydrolysed ferric chloride solutions was achieved by use of a "Millipore" filter using 0.1 micron and 0.4 micron filter discs. The discs are constructed from a plastic material and gave filtration to within close size limits. Filtration was carried out under vacuum.

Experiments as to the effect of irradiation of the solution through glass in contact and out of contact with the solution were carried out, to establish whether a catalytically active film was built up on the surface of the glass. The apparatus used consisted of two 6" diameter evaporating dishes, one being a close fit inside the other. The lower vessel was placed in a thermostat bath with water at 20°C. The solution to be irradiated was placed in this lower vessel. The upper vessel, due to the close fit of the two dishes, when placed on the surface of the solution remained floating and in close contact with the solution. When it was desired to irradiate the solution out of contact with the glass, a glass pillar was inserted between the dishes to hold them apart. Irradiation was carried out through the upper vessel from a G.E.C. 250 watt MED mercury vapour discharge lamp placed vertically above the dishes. The lower vessel had a glass inlet tube inserted at solution level to allow nitrogen to be passed over the surface of the solution when desired.

RESULTS.

Silica gel.

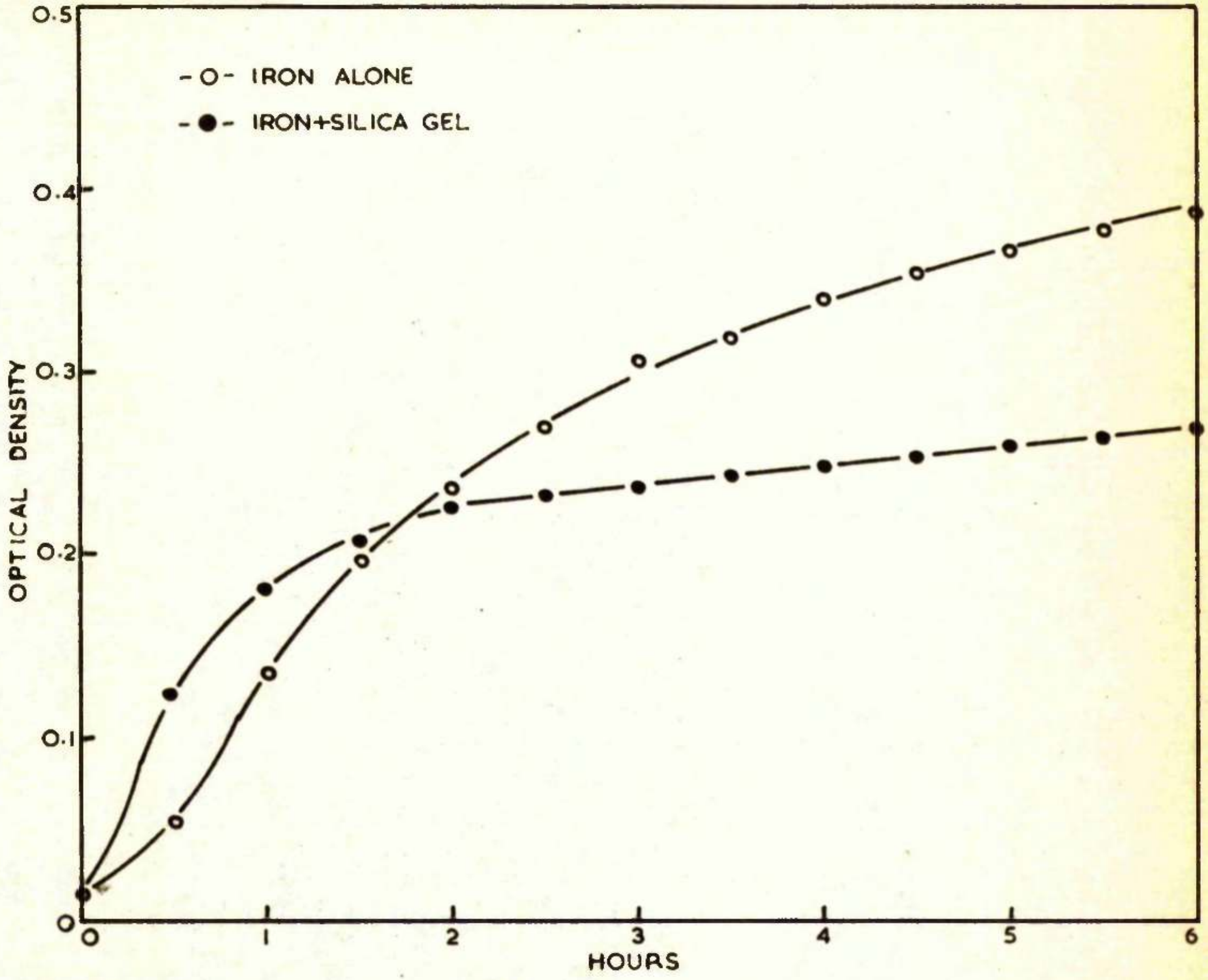
0.5 gms. of silica gel were added to the reaction flask at the commencement of an irradiation run, and the hydrolysis and photo-reduction of the iron measured at half hourly intervals for a period of six hours. The respective results are shown in Figs. 43 & 44, on which are also shown results for neat iron solutions for the purpose of comparison. It is seen that an initial boost in both quantities is replaced as the run progresses by a lowering of the rate.

The above run was repeated, the silica gel being added after the run had progressed with the neat iron solution for one hour, and again in a further run, after three and a half hours. Respective results for hydrolysis and photo-reduction are shown in Figs. 45 & 46, where the initial boost to hydrolysis is in evidence in each case, but there is no boost to photo-reduction, the rate being lowered on addition of the silica gel.

Hydrogen peroxide.

The normal duration of runs was 110 minutes, after which it was found that the peroxide concentration had

FIGURE 43.



HYDROLYSIS CURVES

FIGURE 44.

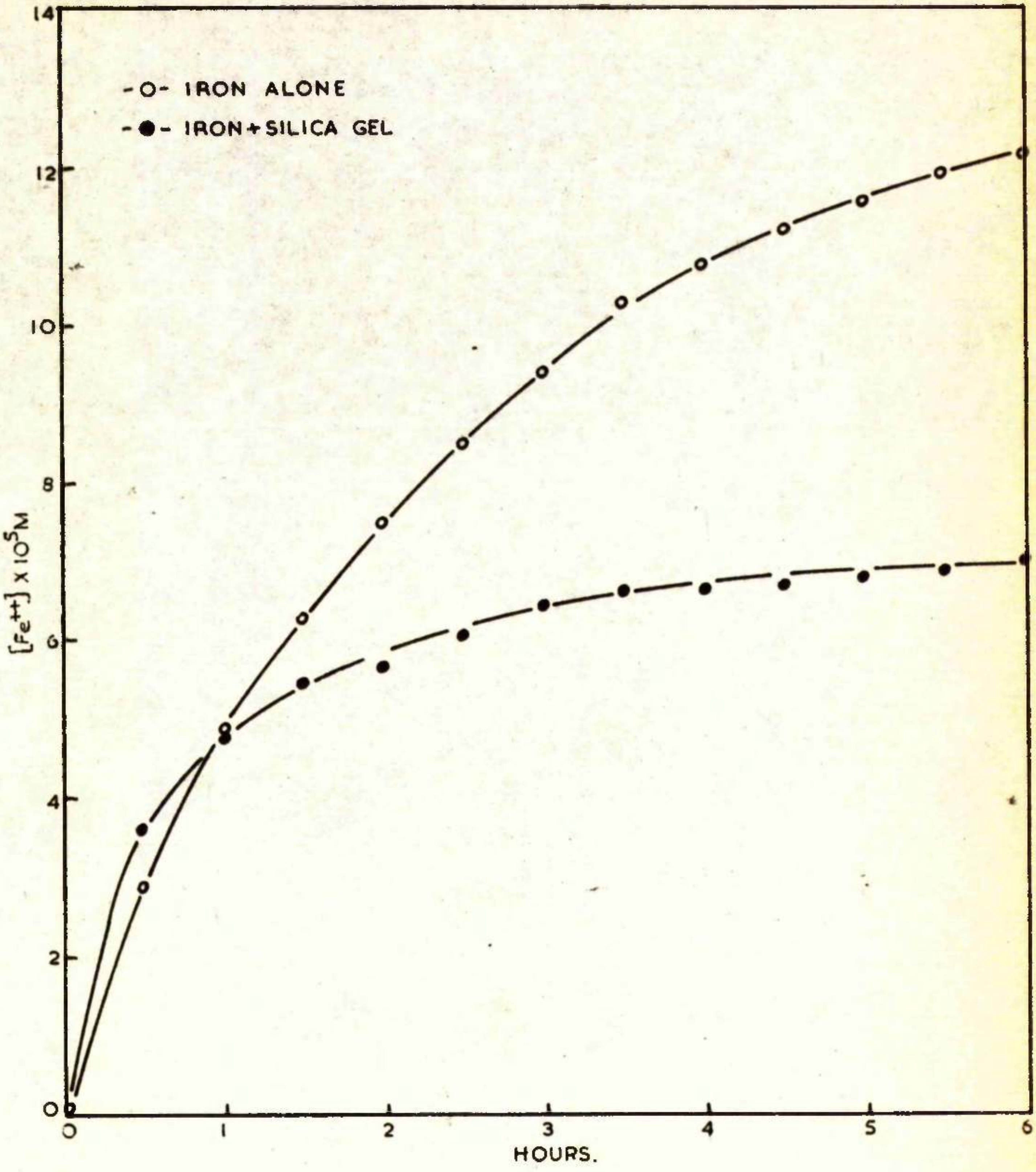
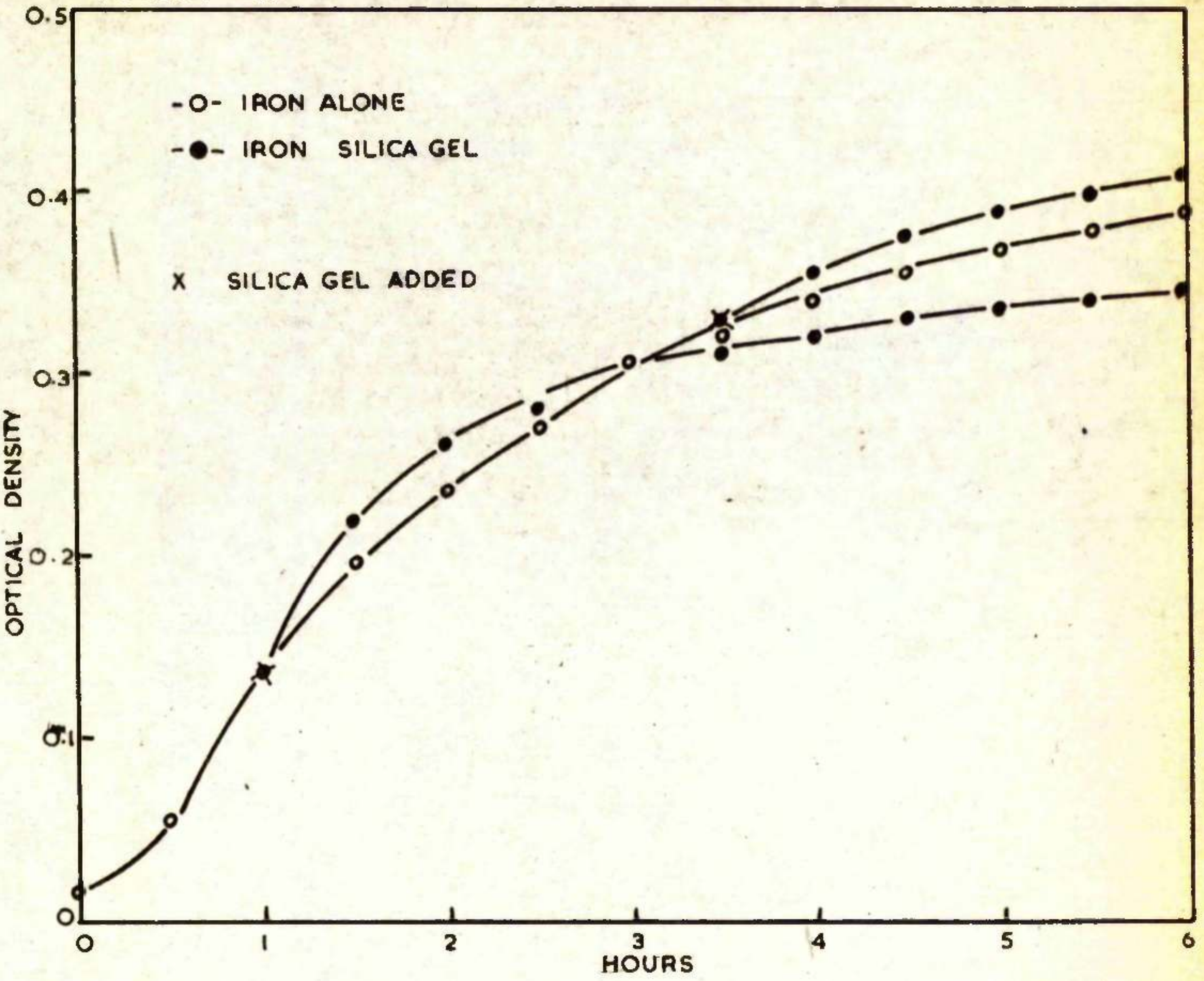


PHOTO-REDUCTION CURVES

FIGURE 45.



HYDROLYSIS CURVES.

FIGURE 46.

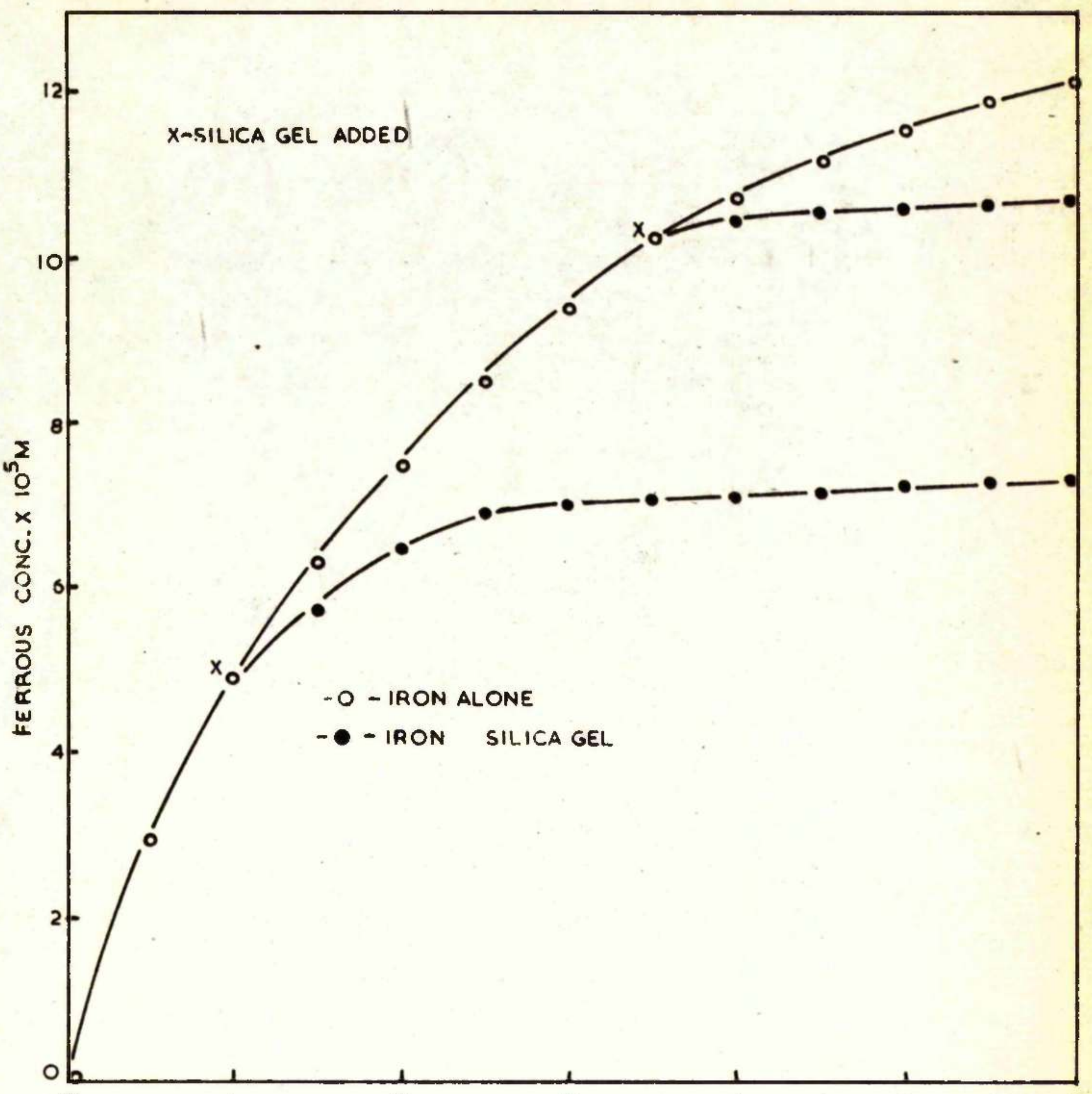


PHOTO-REDUCTION CURVES

fallen to such a level that it was no longer possible to titrate with permanganate to the required degree of accuracy of 2%.

The stock solution of peroxide used was approximately 1.5N and was prepared by adding 30 mls. of the concentrated solution to 970 mls. of distilled water.

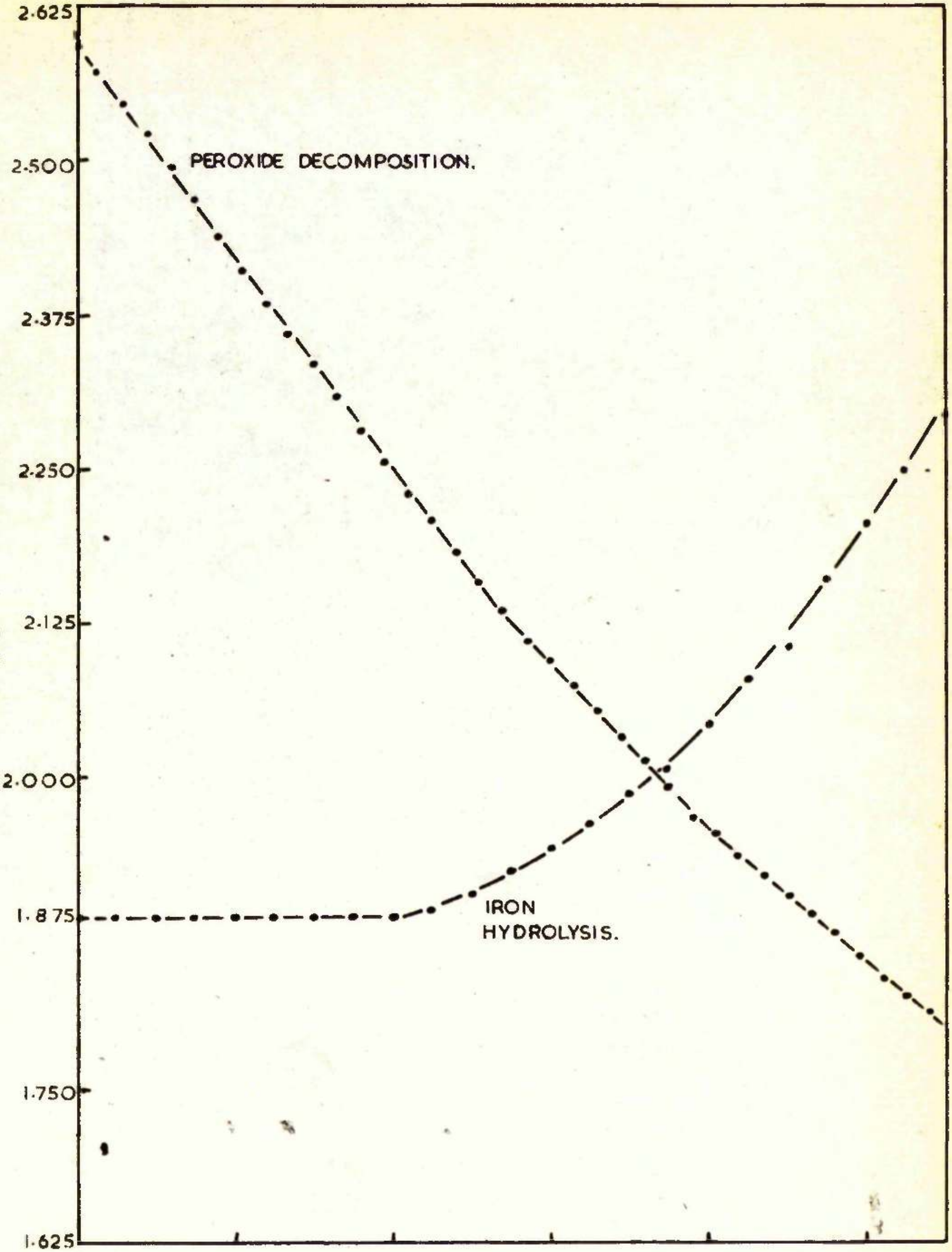
A stock solution of approximately N/5 potassium permanganate was made up and standardised accurately against sodium oxalate solution.

20 mls. of stock peroxide solution were added to 2 litres of distilled water thermostatted at 20°C. into which had been measured 0.4 mls. of ferric chloride melt. 500 mls. of this solution were placed in a blackened flask and 5 ml. samples taken at three minute intervals and placed in titration flasks containing 5 mls. of 3N sulphuric acid, and later titrated against approximately N/50 potassium permanganate solution.

The results are shown in Fig. 47 which is a plot of log(conc. x 10^4M) against time. The run was repeated with continuous stirring of the solution. An identical result was obtained.

It was noticed from the graph that the rate of decomposition appeared to fall into three consecutive

FIGURE 47.

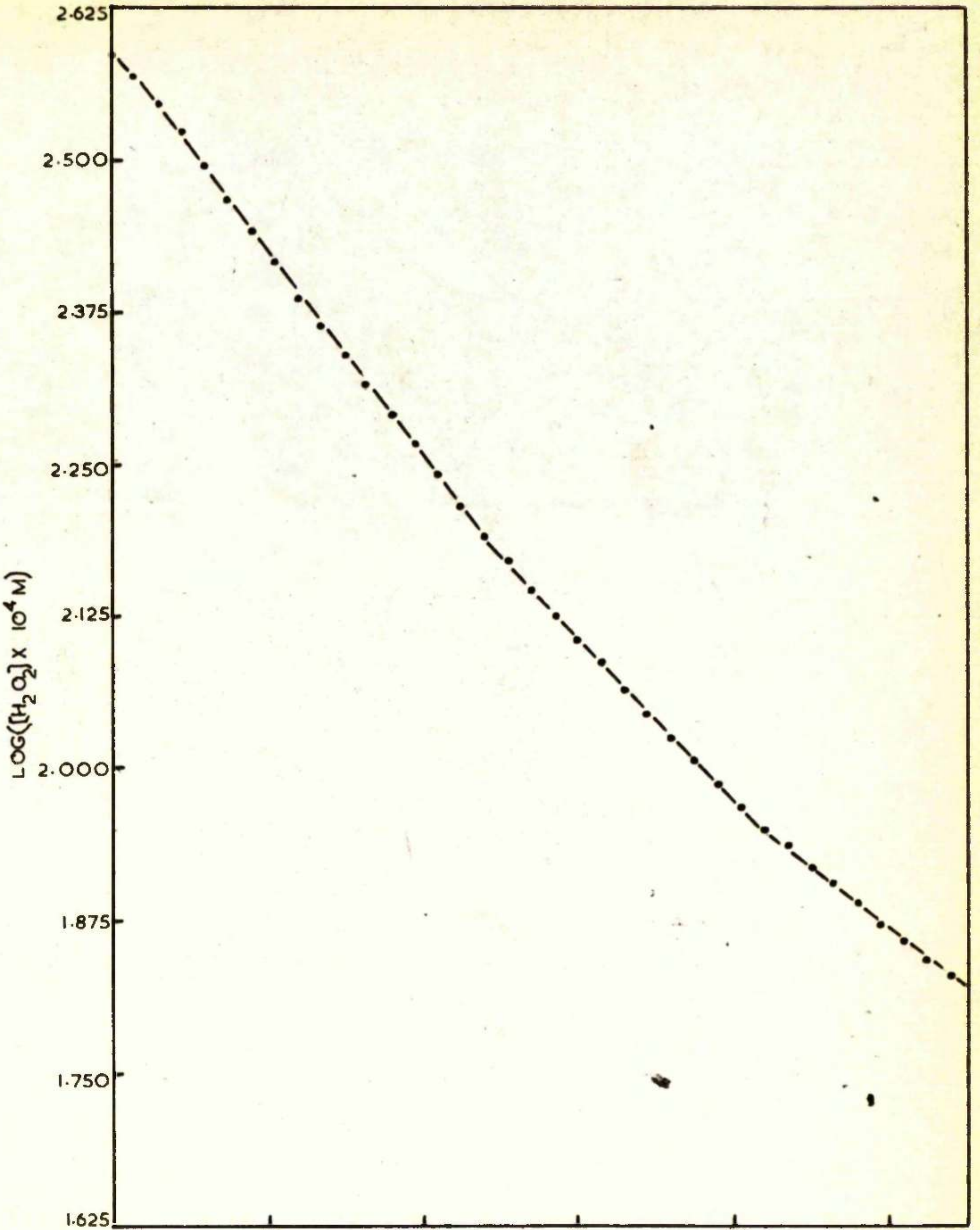


PEROXIDE DECOMPOSITION AND IRON HYDROLYSIS.

first order sections, with distinct changes in the rate at approximately 50 minutes and 80 minutes. As it was known that the onset of secondary hydrolysis took place at about 50 minutes, it was decided to make an accurate measurement of the optical density of the solution at five minute intervals over the first 110 minutes. The measurements were carried out on the "Spekker", using 4 cm. cells and Ilford 601 filters. A plot of the optical density against time is also shown in Fig. 47.

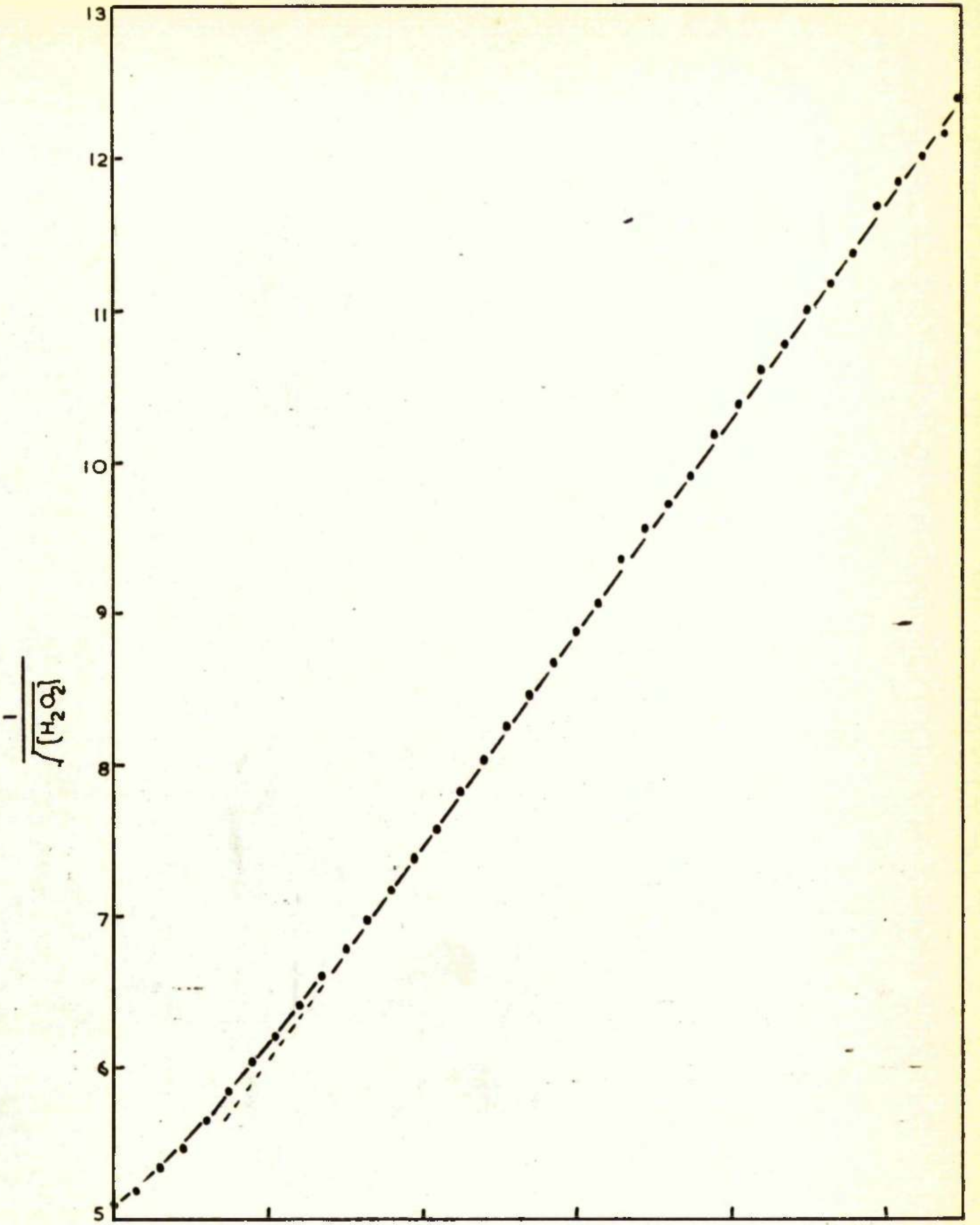
It was found that the onset of secondary hydrolysis appeared about ten minutes before the first break in the rate and hence no direct conclusion could be reached. It was thus decided to carry out a run in which the peroxide was added to an iron solution which had been allowed to age by 40 minutes, so that hydrolysis was due to start at approximately the time of addition of the peroxide to the iron solution. The result is shown in Fig. 48, where it is seen that the breaks in the rate again occur at about 50 minutes and 80 minutes respectively, thus appearing to rule out any effect on the rate caused by the initiation of secondary hydrolysis. A plot was then made of the last run as shown in Fig. 49 in which 1/ /H_2O_2 was plotted against time. It is seen that this plot results in reasonable linearity after the first thirty minutes,

FIGURE 48.



PEROXIDE DECOMPOSITION : H_2O_2 ADDED AFTER 40 MINUTES.

FIGURE 49.



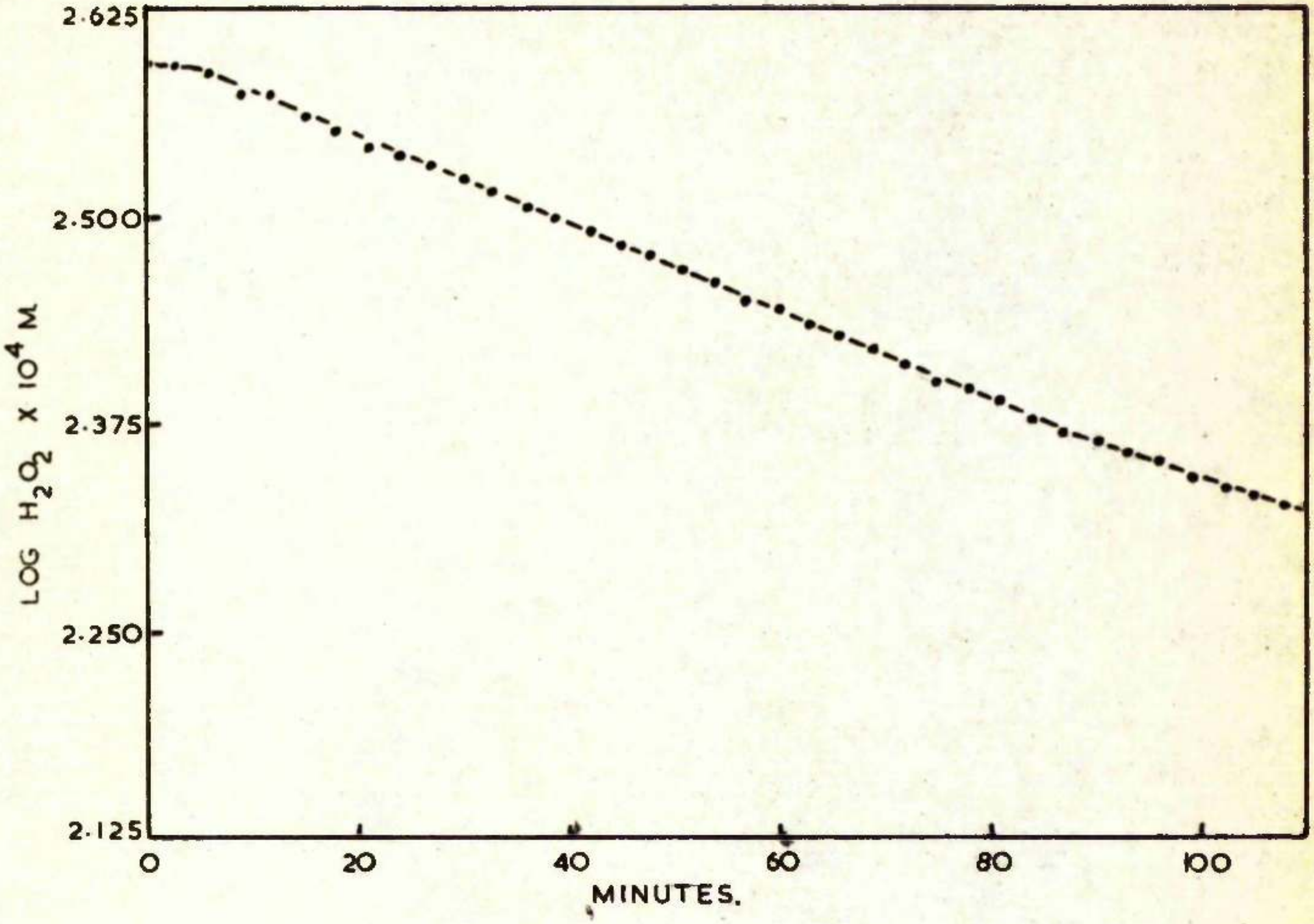
SQUARE ROOT PLOT OF FIGURE 48.

though deviations may still be observed from this linearity throughout the whole plot.

Results for a run in which the peroxide was added to an iron solution aged 24 hours before the addition of peroxide are shown in Fig. 50. In this case the rate changes are again observed at approximately the same times as in the above runs, though the overall rate of the decomposition has been slowed.

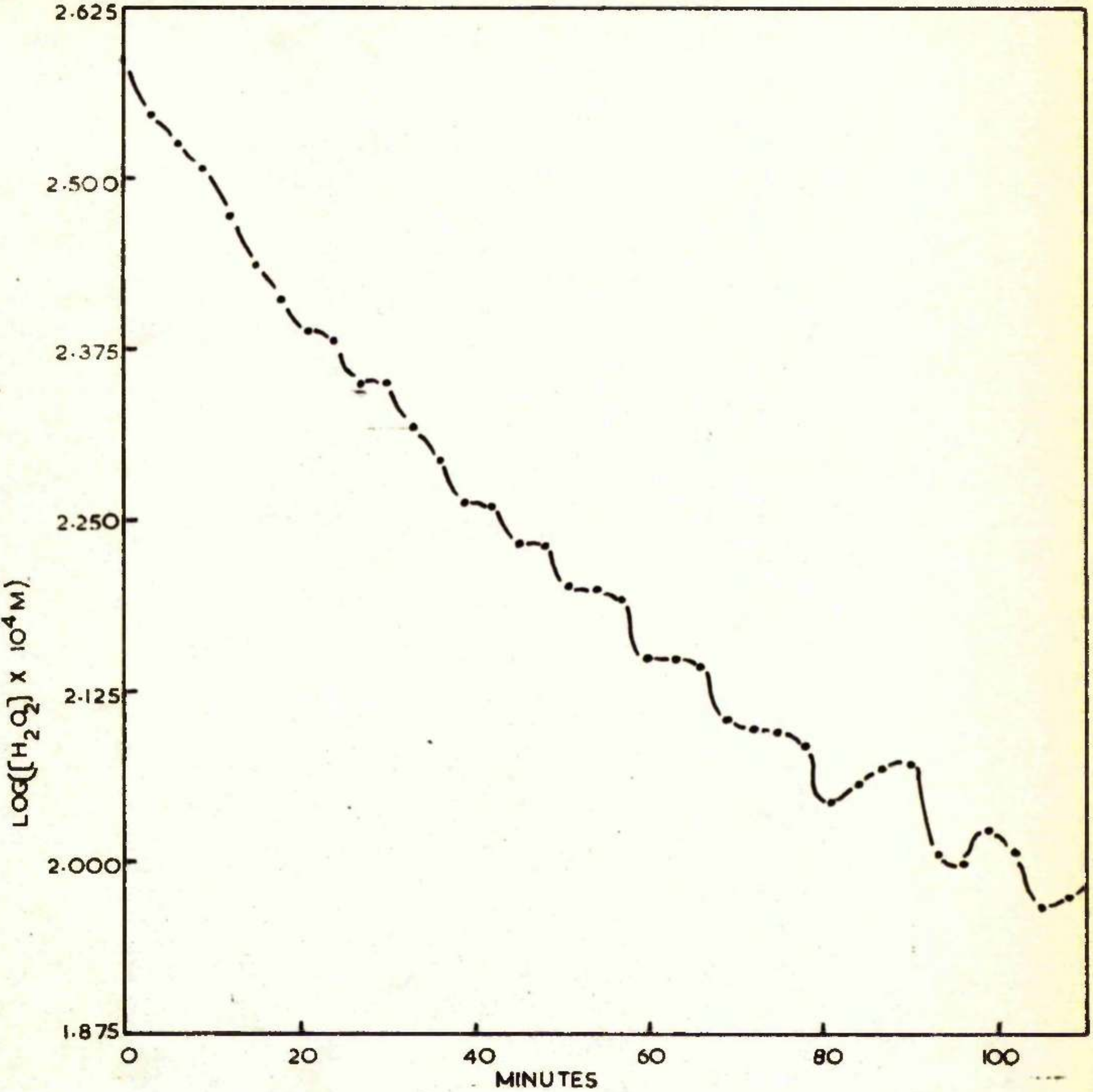
A 1.3 x 10^{-2}M solution of copper sulphate was prepared. 20 mls. of this solution was added to 2 litres of reaction solution as above to give a solution of 1.3 x 10^{-3}M in cupric ion. The run was carried out as above. The results are shown in Fig. 51, where it is seen that on a first order plot in peroxide, the rate of decomposition appears to oscillate, the oscillations becoming more pronounced as the run proceeds. The results of a repeat experiment are shown in Fig. 52, where it is seen that although there is a slight suggestion of the effect, it is not nearly so marked as in the first case. A run was then carried out in which the order of addition of the copper and peroxide was reversed. It was found that in this case there was no oscillating. A repeat run showed a slight trace of the effect. Because of the irreproducibility of the effect, it was decided that it

FIGURE 50.



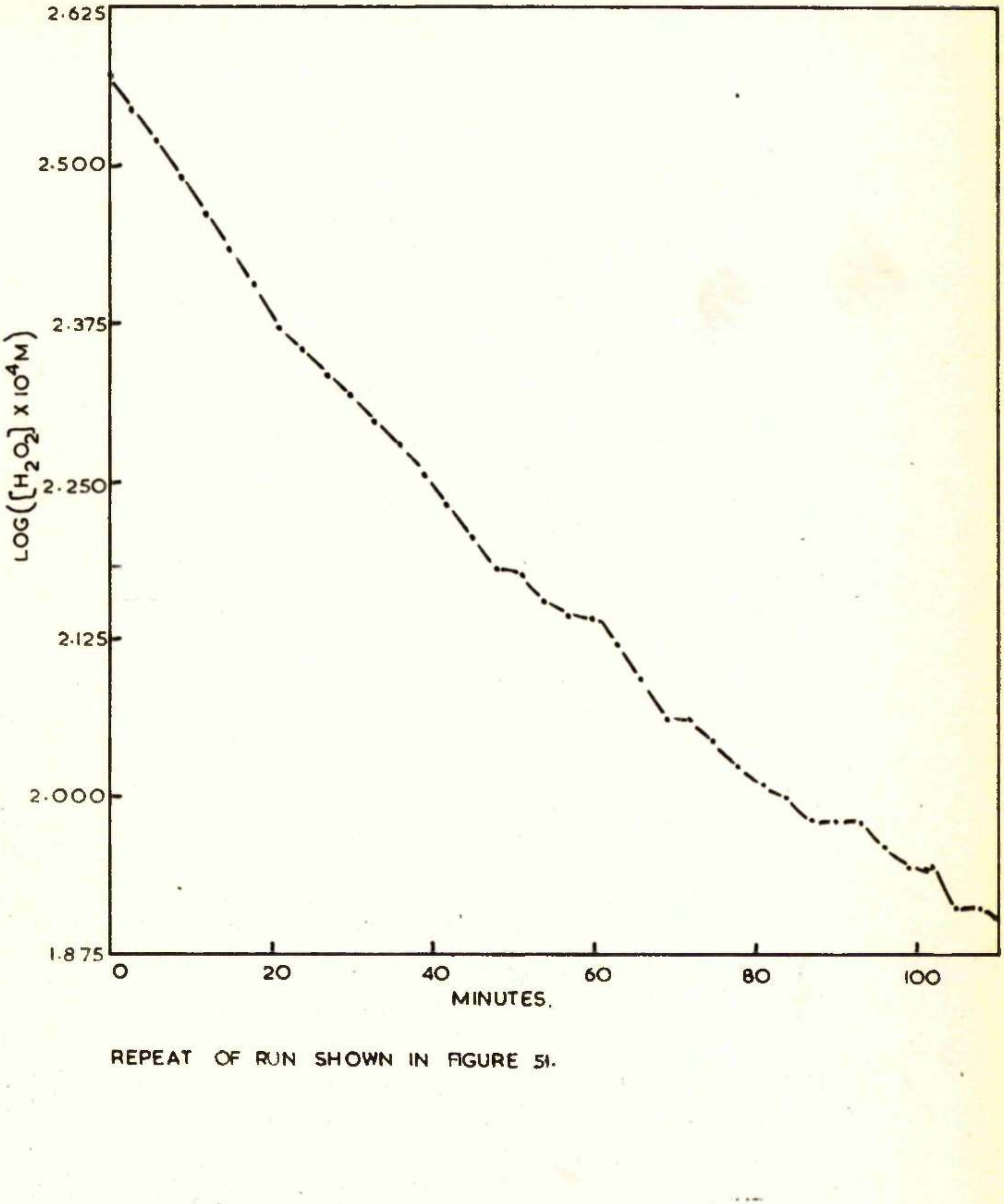
PEROXIDE DECOMPOSITION IN A 24-HOUR OLD FERRIC CHLORIDE SOLUTION.

FIGURE 51.



PEROXIDE DECOMPOSITION IN PRESENCE OF FERRIC CHLORIDE AND COPPER SULPHATE.

FIGURE 52.



REPEAT OF RUN SHOWN IN FIGURE 51.

must be due to some feature of the procedure which it was not found possible to trace. However on numerous runs, graphs of the form shown in Fig. 52 were obtained and thus this was chosen as the one from which to base comparison with the system in absence of cupric ion. It was observed that the average rate of decomposition was somewhat less in the presence of copper, whereas the literature[61] finds that there should be a large increase in the rate of decomposition. At first this was thought to be due to the complexing effect of the sulphate used, and the runs were repeated using cupric chloride and nitrate, the former having the same anion as was employed for the ferric salt, and the latter having an anion of relatively non-complexing properties. Similar results were obtained, and it was thus deduced that this was an inherent property of the system under investigation, perhaps due to a complexing effect by the chloride of the ferric salt itself.

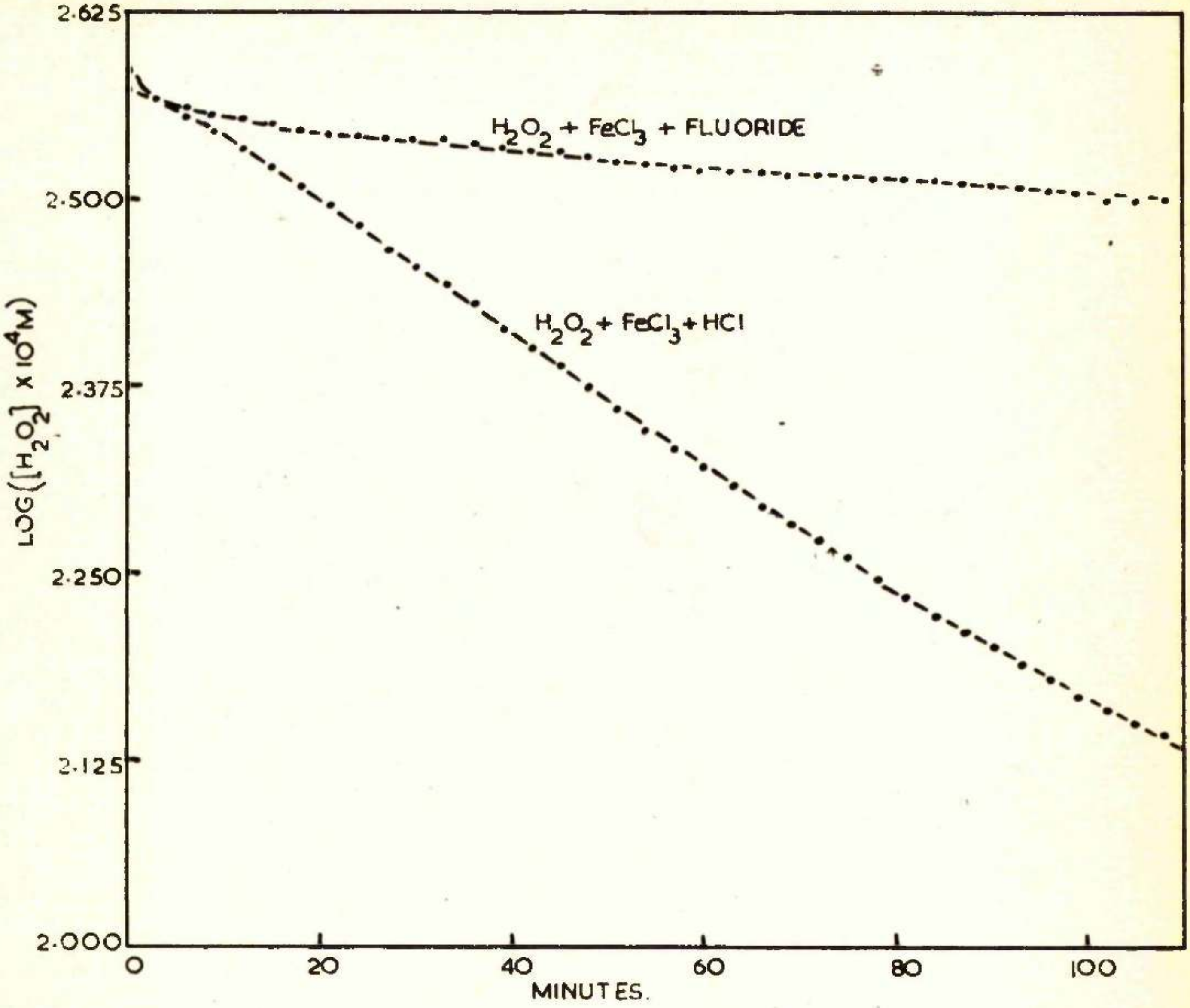
The effect of other complexing agents was tried. 1 ml. of concentrated hydrochloric acid was added to the reaction mixture. The rate was slowed to about half of that found without the addition of the acid, though the breaks in the rate are still in evidence. The decomposition was very markedly slowed by the addition of 10^{-4}M fluoride (as ammonium fluoride). The discontinuity in the rate is not now observed. Both these results are shown in Fig. 53.

Runs in presence of cupric ion were also undertaken at 17°C and 23°C to ascertain whether the oscillations would be aggravated by rise or fall in temperature. There was no evidence of this, though the rate of decomposition is increased by rise in temperature and diminished by fall in temperature.

An iron solution aged 24 hours was filtered through a "Millipore" filter and a peroxide decomposition run carried out on the filtrate. Using the 0.4 micron filter disc, there was no visible residue on the filter and the peroxide decomposition rate was found to be identical to that obtained with an unfiltered iron solution of the same age. With the 0.1 micron disc, however, the filtrate was clear and colourless, having apparently removed all ferric hydroxide particles from the solution. The rate of peroxide decomposition in the filtrate was diminished from that in unfiltered solution as shown in Fig. 54.

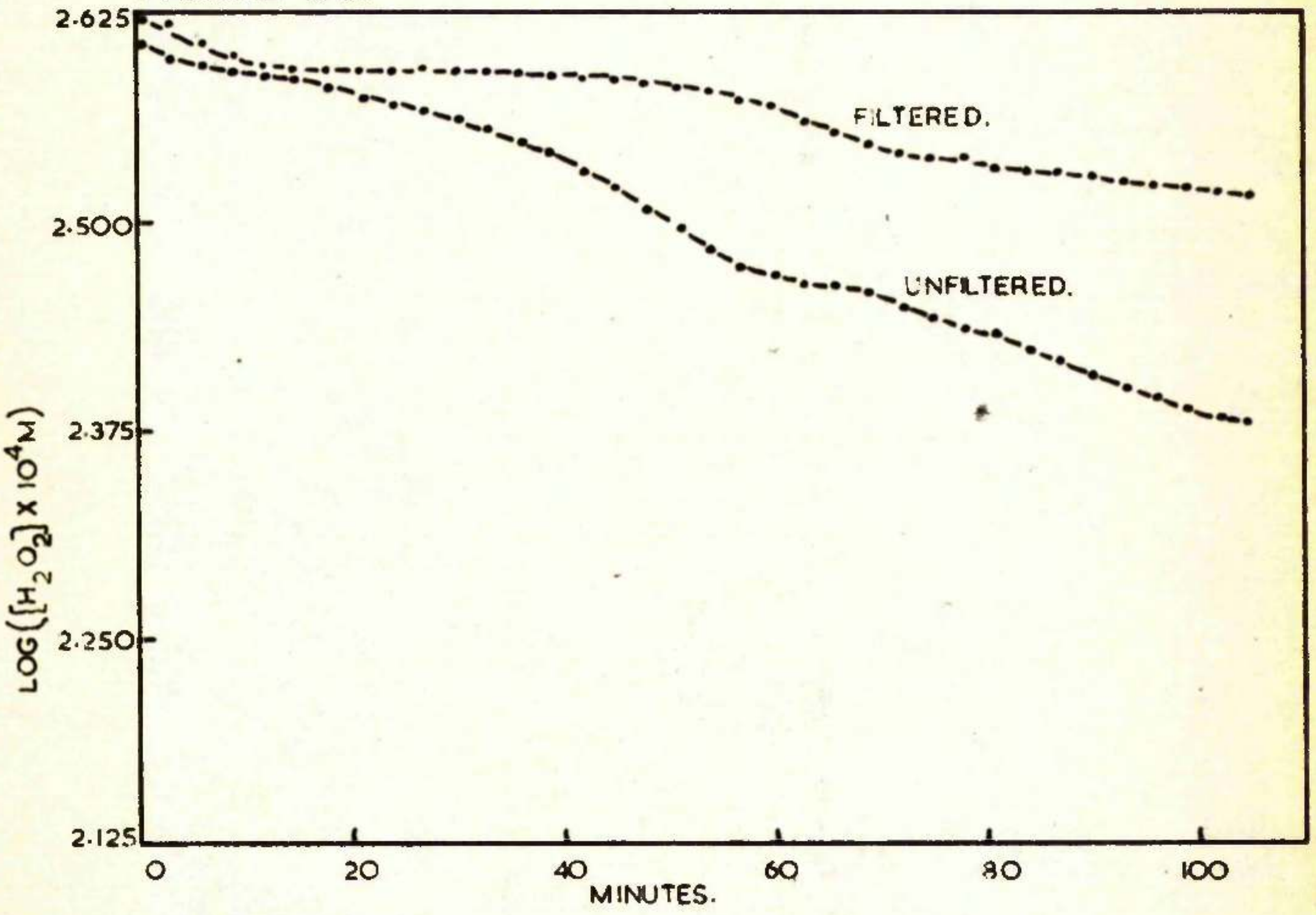
A titanous chloride titration showed that 74% of the ferric iron had been removed by the filtration. The clear filtrate showed no tendency to re-hydrolyse after

FIGURE 53.



PEROXIDE DECOMPOSITION.

FIGURE 54.

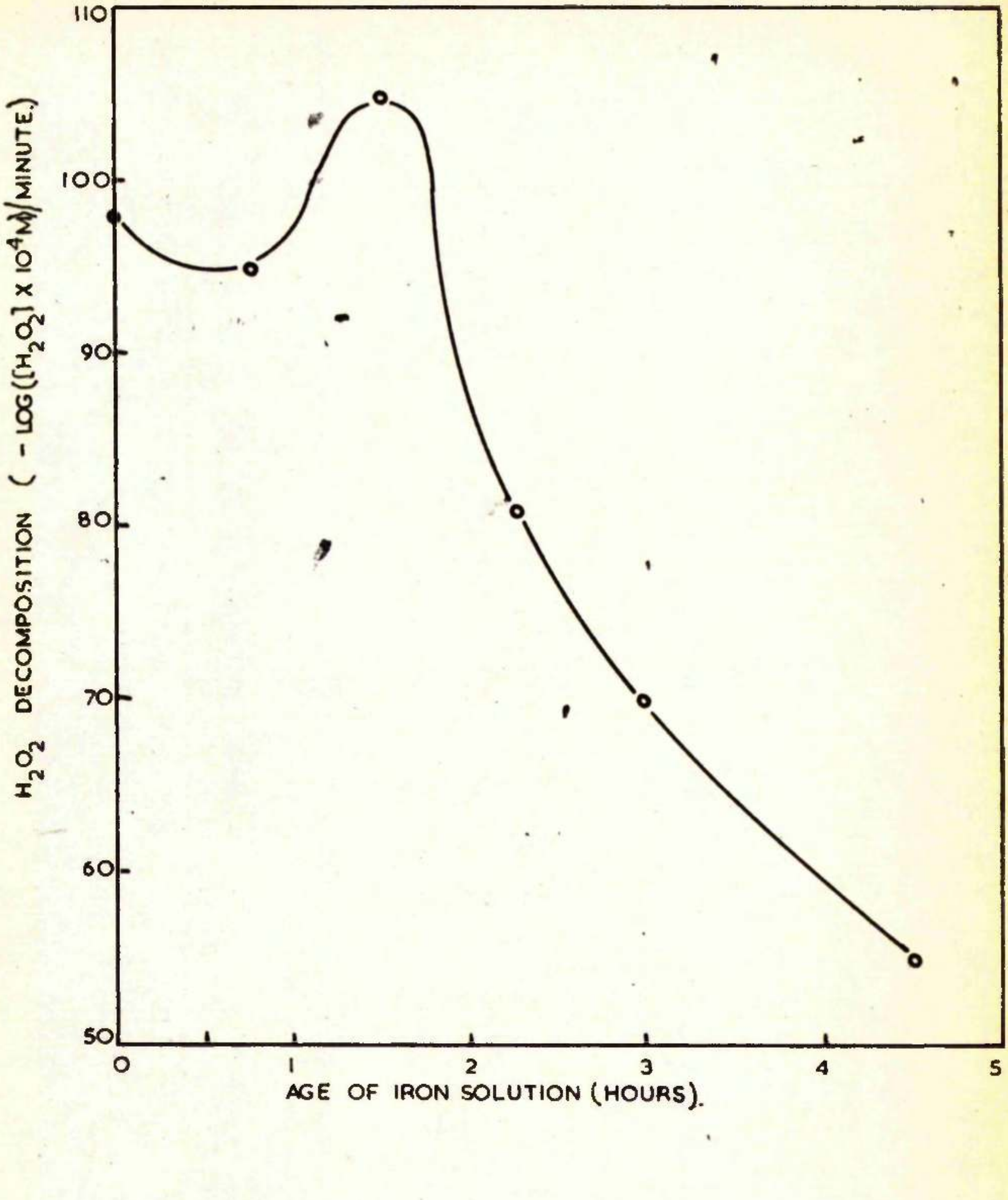


PEROXIDE DECOMPOSITION EFFECT OF FILTRATION THROUGH 0·1 MICRON FILTER.

a period of four days. This is interesting, since Purdon found, as did Lamb and Jacques[39], that the induction period in the secondary hydrolysis is apparent only at concentrations of 1.3×10^{-3}M and higher. Hence in the case of the filtrate from the "Millipore" filter, it would have been expected that there would have been almost instantaneous initiation of the secondary hydrolysis. The explanation is probably that the removal of the basic particles caused the remaining solution to be relatively more acidic than the original solution with respect to the ferric concentration.

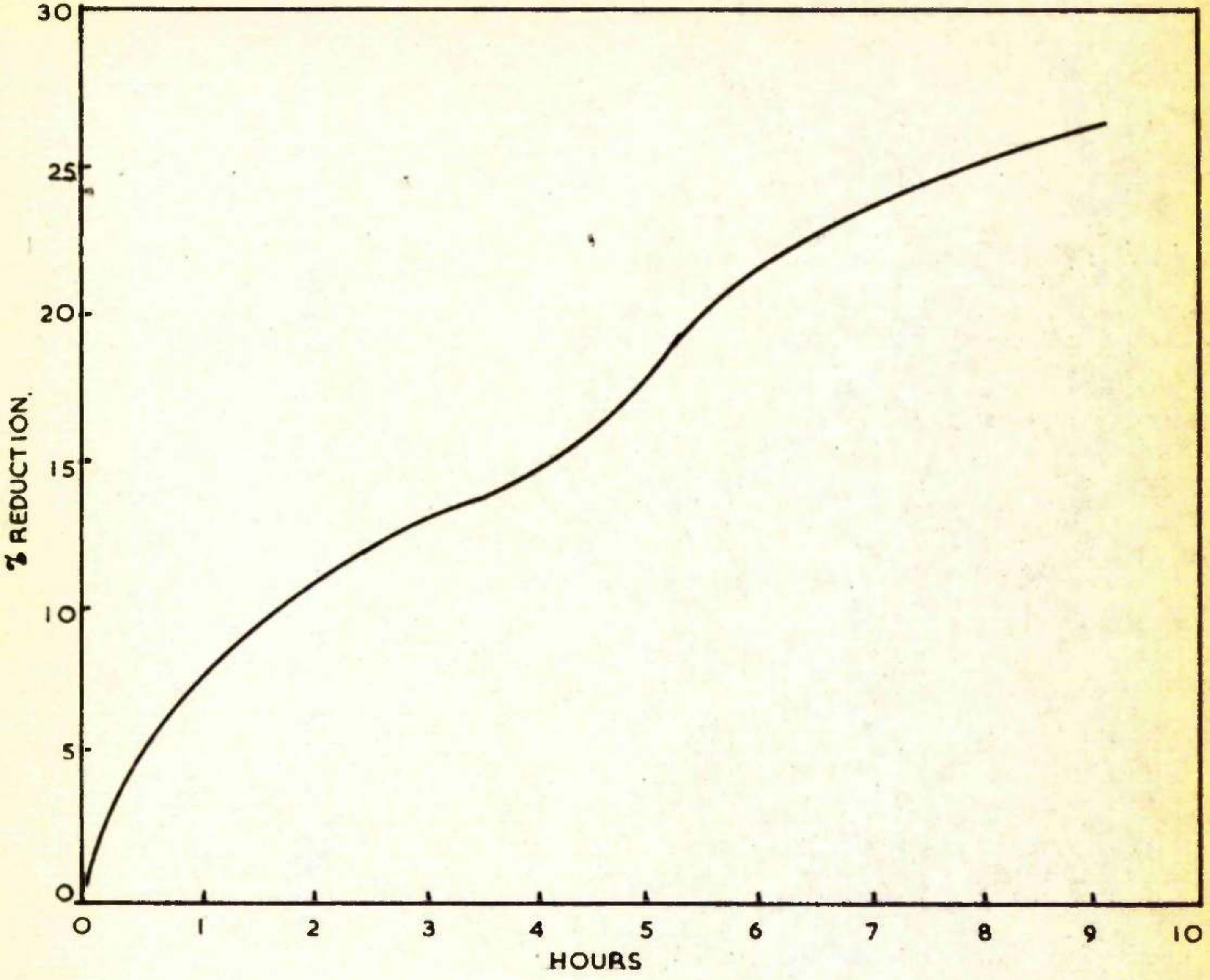
40 minute hydrogen peroxide decomposition runs were carried out on ferric chloride solutions aged 0, ¾, 1½, 2¼, 3 and 4½ hours respectively. The average gradient of each decomposition curve was measured and plotted against time as shown in Fig. 55. There is seen to be a maximum in the curve as 1½ hours, corresponding to a maximum activity in peroxide decomposition at this time. It is interesting to note that on irradiation of a ferric chloride solution, brought to a pH of 2.89 by addition of hydrochloric acid, Purdon obtained a boost in photoactivity after about 4 hours irradiation (Fig. 56). This boost in activity would seem to be of the same

FIGURE 55.



PEROXIDE DECOMPOSITION IN IRON SOLUTIONS OF VARIOUS AGES.

FIGURE 56.



BOOST IN PHOTO ACTIVITY IN SOLUTIONS OF pH 2·89
(AFTER PURDON.)

nature as the boost demonstrated in Fig. 55. Repeat runs yielded similar results.

The above experiment was repeated using an iron solution of pH 2.89. No boost in activity was observed after 4½ hours, during which time the activity remained constant at a gradient of -79log H_2O_2 x 10^4M / minute. There was however a boost after 24 hours to a value of gradient of -86log H_2O_2 x 10^4M / minute, beyond which time there was a fall in rate to -75log H_2O_2 x 10^4M / minute after a period of 5 days.

The optical density of the various solutions was measured and three values are given below.

pH	age of soln.	irradiation	O.D.
3.05	1½ hours	dark	0.195
2.89	24 hours	dark	0.187
2.89	4½ hours	U.V.	0.194

It is seen that in each case the boost in activity occurs when the solutions have reached a comparable degree of hydrolysis as measured by the optical density.

Experiments were carried out to establish the effect of an iron film on the surface of the reaction vessel to determine whether it could be catalytically active in the photo-activity of the solution.

The apparatus used has been described on a previous page(129). A photo-reduction run was carried out with the solution in contact with the glass face of the reaction vessel through which the light was falling. The run was repeated with the solution out of contact with the face of the vessel. The results are shown in Fig. 57, where it is seen that when the solution is in contact with the face of the vessel, there is an increased photo-activity, suggesting that the surface of the vessel is catalytically active in the photo-reduction process. A run was carried out in which the solution was out of contact with the face of the vessel, and a stream of nitrogen was passed over the surface of the solution. The result obtained was identical to that obtained under the same conditions without the passage of nitrogen.

FIGURE 57.

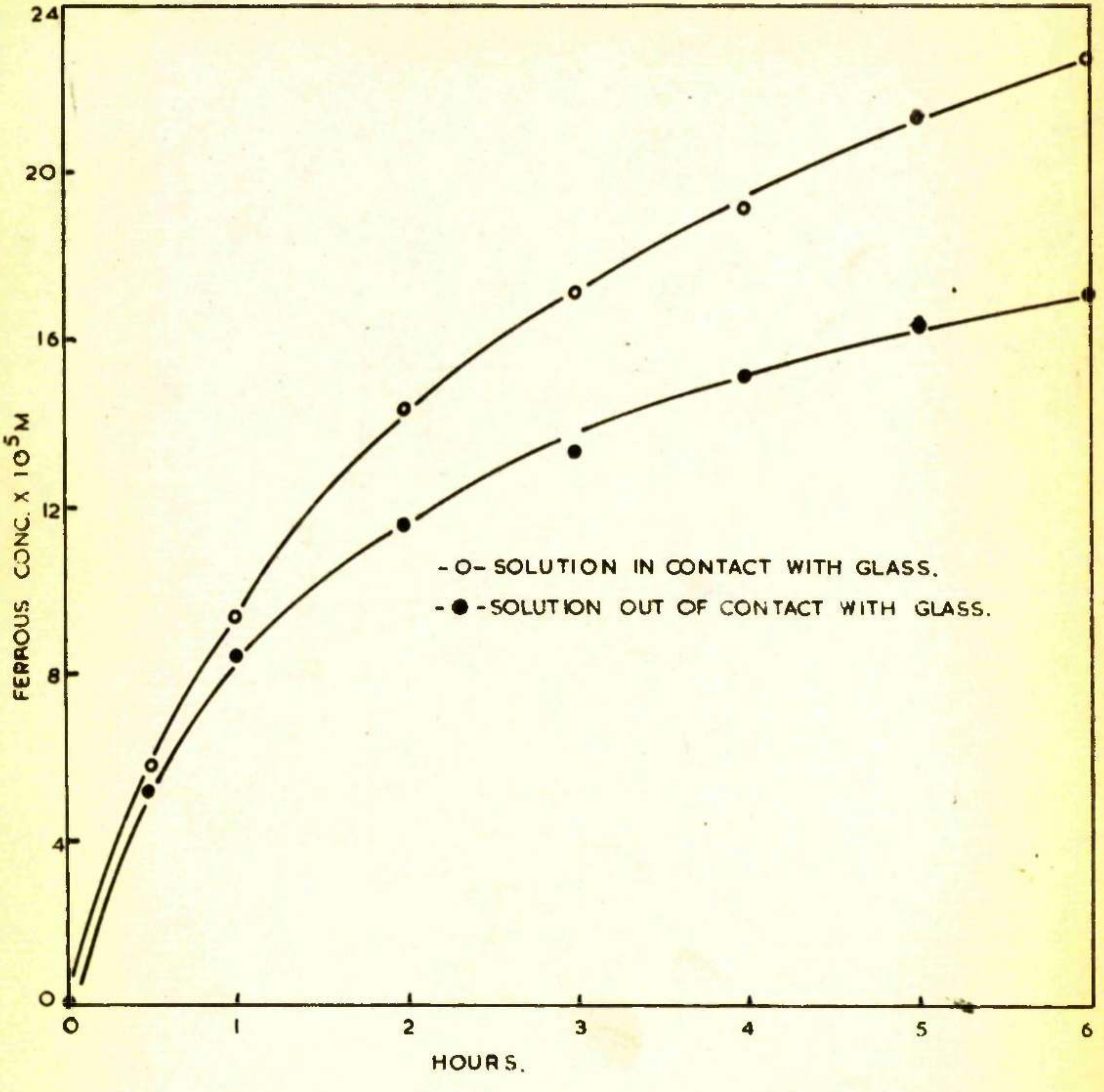


PHOTO-REDUCTION CURVES.

DISCUSSION.

The results with the silica gel would tend to indicate that the photochemical reaction is of a heterogeneous nature, taking place at the surface of particles in the solution. When silica gel is added to the solution, there is an initial boost to the photo-activity. However this boost soon disappears and the ensuing rate is less than normal. A probable explanation of this lowering of the rate is that the silica gel adsorbs ferric hydroxide, poisoning the silica gel surface, and at the same time, removing the finely divided colloidal ferric hydroxide particles from their active state. The boost in photo-activity is not observed when the silica gel is added to solutions which have been allowed to age for one hour or more before addition of the gel. By this time the solutions have reached their maximum activity with regard to ferric hydroxide particles, and thus it is to be expected that the activity would be reduced by the addition of silica gel which removes the active particles.

The initial boost to hydrolysis is due to an aggregation of ferric hydroxide particles already formed, to more massive form on the surface of the silica gel, rather than to an increase in the rate of the actual secondary hydrolysis. This is demonstrated by the fall in the rate of hydrolysis after 2 hours. The fact that this fall does not occur when the silica gel is added after 3½ hours is due to the relatively slow rate of hydrolysis prevailing in the solution at that time.

Hydrogen peroxide.

Under the conditions of the present investigation, the decomposition of hydrogen peroxide has been shown to take place in a sequence of first order steps of decreasing rates. Since the molar ratio of H_2O_2 / Fe^{3+} did not fall below unity, even at the end of the first hundred minutes of reaction, a first order decomposition is in agreement with the results of Barb et al.[49]

There would appear to be an induction period in the first ten minutes of the decomposition during which the rate increases to its maximum value. This might possibly be attributed to the breaking down of complexes formed by the hydrogen peroxide with the ferric ion.

It is suggested that the segmentation of the plot may be due in some way to the changing nature of the catalyst as a result of hydrolysis.

It was seen that the first break occured at about the time of initiation of secondary hydrolysis in a freshly prepared iron solution. This would indicate that the formation of colloidal particles was influencing the reaction rate. However this explanation seems unlikely on consideration of the results obtained on aged iron solutions, since here the colloidal particles have already formed prior to the addition of peroxide, and the breaks in the rate are still observed.

Also, from consideration of Fig. 55 it would be expected that any rate change observed over the first hundred minutes of reaction would occur as a speeding up rather than a slowing down of the rate, since the maximum photo-activity occurs in solutions aged 90 minutes.

Milloy found that the hydrolysis of ferric chloride solutions in the light was increased by the addition of hydrogen peroxide, provided that hydrolysis had already commenced by the time the peroxide was added. Initially added peroxide caused a retardation of the commencement of hydrolysis, which however after commencement, proceeded at a rate slightly greater than that in the absence of peroxide.

No completely satisfactory explanation was found for this increase in hydrolysis by the addition of peroxide.

It is now suggested that this effect of increased optical density is due, not to an increase in the actual hydrolysis of the ferric chloride, but to partial aggregation (resulting from the breaking down, by the action of the peroxide, of the zeta potential) of the colloidal particles already present. That this could take place was demonstrated by the effect of peroxide on the film electrode as shown in part 1 (page 51) of this work. The puzzling fact remains, however, that there is no observed increase in optical density in presence of peroxide in the dark.

The explanation of the reduction in rate of the peroxide decomposition would thus appear to be due to the aggregation of particle size by the peroxide beyond the optimum for catalysis.

The results with the "Millipore" filter show that the particle size in a hydrolysed solution lies between 0.1 and 0.4 microns, and after 24 hours, 74% of the ferric iron solution has hydrolysed to colloidal ferric hydroxide.

There is a diminution of rate of decomposition of peroxide on removal of the colloidal particles, possibly due to the increased ratio of hydrogen ion to ferric ion in the resulting solution, but also indicating that the particles do indeed catalyse the reaction which is thus of a heterogeneous nature.

This is borne out by the increase in photo-reduction obtained when the solution is irradiated through a glass surface in contact with the solution. As was seen in part 1 of this work, a film builds up on the surface of the glass. Since there is an increase in the formation of ferrous ion, the film is assumed to be catalytically active, and thus in the bulk of the solution, the catalytically active sites are the surfaces of the colloidal particles. Only those in close proximity to the surface of the vessel will be active, due to extinction of the active radiation on passage through the solution - hence the noticeable activity of the film on the surface of the glass, despite its large reduction in active surface area from that of the particles, by deposition on the glass.

That there is an optimum particle size is demonstrated by the results in the table on page 138 where in each case a boost of activity is shown where the optical density of the solution is about 0.19.

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