SOME PHOTOCHEMICAL PROPERTIES

of

FERRIC IRON SOLUTIONS

A THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the

requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

WILLIAM A. B. PURDON.

September, 1956.

ACKNOWLEDGMENTS.

The author wishes to record his very sincere thanks to Dr. William Good for his helpful, critical and inspiring discussions and to acknowledge with gratitude the receipt during the course of this work of a maintenance allowance from the Department of Scientific and Industrial Research.

SUMMARY AND GENERAL CONCLUSIONS.

pH

Solutions of $1.3 \times 10^{-3}\bar{M}$ ferric chloride of p_H between 2.0 and 3.05, and in the absence of added substrate are found to be photo-active. The photo-activity is to be attributed to the 'dimer' $Fe_2(OH)_2^{+4}$ and possibily also to the species $Fe^{+3}OH^-$.

Experimental proof of OH radical formation is shown by the hydroxylation of substrates benzene and benzoic acid, which are oxidised to phenol and salicylic acid respectively.

Experimental evidence is adduced to show that the photo-activity is not due to oxidisable organic impurities in the distilled water. Possible processes are oxidation of chloride to chlorine and/or oxidation of water to oxygen.

No chlorine was found with a sufficiently sensitive test. In fact, irradiation of Fe^{+3}/Cl_2 solutions leads to the disappearance of chlorine.

Using the 'freezing and thawing' technique of Dain and Kachan for measurement of small quantities of gas, a non-condensible gas was found to be photo-produced in these iron solutions. The amount of gas was shown to accord with the stoichiometry of the equation:-

$$Fe^{+3} + \tfrac{1}{2}H_2O \longrightarrow Fe^{+2} + \tfrac{1}{4}O_2 + H^+$$

Further, the gas was identified as pure oxygen by

(a) the phosphor method of Kautsky and Hirsch,

(b) sparking with hydrogen, resulting in a 2/1 combination.

The photo-oxidation of water by ferric ion is thus established.

The following reaction scheme is proposed. -

$$\begin{aligned}
&Fe_2(OH)_2{}^{+4} &&\xrightarrow{h\nu} && Fe^{+3}OH^- + Fe^{+2} + OH\\
&Fe^{+2} + OH &&\longrightarrow && Fe^{+3} + OH^-\\
&Fe^{+3}OH^- + OH &&\longrightarrow && Fe^{+2} + H_2O_2\\
\text{or}\quad &OH + OH &&\longrightarrow && H_2O_2\\
\text{and}\quad &H_2O_2 &&\xrightarrow[\text{iron catalysis.}]{} && H_2O + \tfrac{1}{2}O_2.
\end{aligned}$$

The quantum yield of Fe^{+2} formation

$$(\gamma_{Fe^{+2}})_{max.} = .026$$

Powdered silica was found to provide an active surface for the increase in photo-reduction of Fe^{+3}. In the analogous ceric cerous system Dain and Kachan suggest that the increased photo-activity is due to a recombination of OH radicals on the surface of the silica, leading to a higher oxygen yield.

It was shown in the present work that a 'fresh' surface of colloidal ferric hydroxide increases the photo-reduction of the iron. It is suggested that this is due to some 'dark' heterogeneous reaction such as the recombination of OH radicals or catalysis of some electron-transfer reaction, which would in time increase the oxygen yield.

The effect of light intensity (365 mμ) was measured. The initial $(\frac{dFe^{+2}}{dP}) \propto \sqrt{I}$. However, the maximum yield i.e. $[Fe^{+2}]_{stationary}$ *is* a linear function of $\sqrt{I}$. Relatively high intensities are therefore necessary for easily measurable oxygen evolution, a suggestion already made by Uri.

Light was found to initiate and accelerate the process of secondary hydrolysis of the iron to $Fe(OH)_3$, as compared with the dark hydrolysis. Experimental results point to the conclusion that the reaction, $Fe^{+2} + H_2O_2$ is basically responsible for the phenomenon, and provide further, independent evidence that H_2O_2 is present in the system $Fe^{+3}/U.V.$

INDEX.

GENERAL INTRODUCTION.

A. Free Radicals.

The importance of the role of unstable intermediates in the mechanism of reactions in both gas and liquid phases has only recently been realised. These intermediates are free neutral atoms or radicals or ionic species. Only a few such intermediates have been isolated in a pure state. Their existence is generally deduced from kinetic measurements, absorption spectra, electrical conductivity, magnetic susceptibility etc.

Free radicals or radical-ions or odd ions (free unpaired electron) enter into reactions with a low heat of activation and appear in low stationary concentration in pseudo equilibrium.

The monographs of Steacie[1] and Waters[2] are mainly concerned with organic free radicals. In the review by Uri[3], "Inorganic Free Radicals in Solution", reactions are dealt with which involve inorganic ions or radicals in the primary step.

Important free radicals in many reactions are those formed from hydrogen and oxygen. These are discussed below followed by a general survey of inorganic free radical reactions both thermal and photochemical.

(1). The HO_2 radical and the O_2^- radical-ion.

The existance of the perhydroxy radical HO_2 was first suggested by Taylor[4], and it is assumed to play an essential part in the reaction between hydrogen and oxygen. Haber[5] suggested that the radical is formed when hydrogen atoms, formed in a discharge tube, react with molecular oxygen in the presence of a third body. An unstable product from this reaction, having an atomic ratio of one of hydrogen to one of oxygen, was isolated by Geib and Hartek[6], working at low temperature. There is very strong evidence for the existance of HO_2 from studies of gas phase reactions above 400°C.[7,8]. Eltenton[9] used a mass spectrometer to examine low pressure flames of oxygen and methane and propane, and the results indicated the formation of HO_2 radicals during the course of the reactions. The photochemical formation of hydrogen peroxide from hydrogen and oxygen both in the presence and absence of excited mercury atoms has been interpreted as due to the formation and interaction of HO_2 radicals[10]. The cause of the inhibition by molecular oxygen of the photochemical reaction between hydrogen and chlorine is attributed to the production of these radicals[11].

Minkoff[12] has reviewed the evidence for the existence of the HO_2 radical in the gas phase.

The O_2^- ion is the anion of the free radical HO_2. Potassium superoxide, which was originally given the structure M_2O_4[13], is paramagnetic and the X-ray study of its crystal structure by Helms and Klemm[14] revealed that the correct formula was MO_2 (M = potassium, rubidium, caesium). This was confirmed more recently by Kassatochkin[15], who with Kotov[16] had previously suggested the structure MO_2. In aqueous solution it is postulated that the HO_2 radical is dissociated to $H^+ + O_2^-$ [17,18,19].

The decomposition of ozone in aqueous solution was studied by Weiss[17]. It was shown this can be accounted for by a chain reaction involving HO_2 and OH radicals, catalysed by OH^- ion.

$$\begin{array}{lllll}
O_3 + OH^- & \longrightarrow & O_2^- & + & HO_2 \qquad \text{initiating step.} \\
O_3 + HO_2 & \longrightarrow & 2O_2 & + & OH \\
O_3 + OH & \longrightarrow & O_2 & + & HO_2 \\
HO_2 + OH & \longrightarrow & O_2 & + & H_2O \\
HO_2 + HO_2 & \longrightarrow & O_2 & + & H_2O_2
\end{array}
\begin{array}{l}
\\
\left.\begin{array}{l} \\ \\ \end{array}\right\} \text{chain propogation.} \\
\left.\begin{array}{l} \\ \\ \end{array}\right\} \text{termination.}
\end{array}$$

The reaction between ozone and hydrogen peroxide was explained quantitatively on this basis by Taube and Bray[20].

Franck and Haber[21] were the first to treat the process of aerobic oxidation on the basis of modern concepts of free radical production by electron transfer. The example chosen by them was the autoxidation of sulphite ion initiated by traces of cupric ion. A slightly modified mechanism involving the HO_2 radical was suggested by Weiss[22] on the basis of the results obtained by Goldfinger and Graf von Schweinitz[23] and by Haber and Wansbrough-Jones[24]. Weiss[25] proposed that there is an electron transfer from reducing agent to oxygen forming the molecular oxygen ion which is in equilibrium in aqueous solution with the perhydroxy radical.

$$O_2^- + H_3O^+ \rightleftharpoons HO_2 + H_2O$$

Thus the formation of hydrogen peroxide found in many of these reactions can be explained.

$$O_2 + e \longrightarrow O_2^-$$

$$HO_2 + e \longrightarrow HO_2^-$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2$$

Similarly the traces of ozone sometimes found[26] can be explained

$$2HO_2 \longrightarrow H_2O + O_3 .$$

One may take as examples the auto-oxidation of metal ions and of leuco -dyes.

In the case of metal ions in solution Weiss[25] suggested the following mechanism for the auto-oxidation of ferrous ion.

$$Fe^{+2} + O_2 \rightleftharpoons Fe^{+3} + O_2^-$$
$$O_2^- + H^+ \rightleftharpoons HO_2$$
$$Fe^{+2} + HO_2 \rightleftharpoons Fe^{+3} + HO_2^-$$
$$HO_2^- + H^+ \rightleftharpoons H_2O_2 .$$

The auto-oxidation of leuco-indophenols was studied by Baxendale and Lewin[27]. The conclusion was drawn that QH^- was the reducing species. QH^- is formed by the ionic dissociation of the leuco-indophenol

$$QH_2 \rightleftharpoons QH^- + H^+$$

the rate determining step is assumed to be

$$QH^- + O_2 \longrightarrow Q^- + HO_2$$

or $$QH^- + O_2 \longrightarrow QH + O_2^-$$

On the basis of this work Evans[28] built the hypothesis of the linear relationship of the free energy of reaction and of activation in electron transfer reactions.

A complete analysis of the aerobic oxidation on the basis of the semi-quinone theory, including the effects of catalysis and inhibition (particularly by metal ions) has been put forward by Lu Valle and Weissberger[29,30].

(2). The OH Radical.

The hydroxyl radical, OH, was postulated by Bonhoeffer and Haber[31], Farkas, Goldfinger and Haber[32] and Haber[5] in the reaction between hydrogen and oxygen. In the decomposition of water vapour its occurrence was assumed by Bonhoeffer and Reichardt[33]. Urey, Dawson and Rice[34] postulated the OH radical in a study of the absorption spectrum of hydrogen peroxide in the gas phase and in solution. The absorption spectrum of OH radicals in the gas phase was investigated by Oldenburg and Reike[35,36] with a high resolving spectroscope.

Hinshelwood[7], in his Bakerian lecture (1946), said that the reactions between hydrogen and oxygen involved the following elementary steps with H, OH and HO_2 radicals as the intermediates

$$H_2 \longrightarrow 2H$$

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

$$H + O_2 \longrightarrow OH + O$$

$$O + H_2 \longrightarrow OH + H$$

$$H + O_2 + (M) \longrightarrow HO_2 + (M)$$

$$HO_2 + H_2 \longrightarrow H_2O + OH.$$

The photochemical decomposition of hydrogen peroxide in solution 1 studied by Kornfield[37] and Lea[38], is postulated as a chain reaction consisting of the following steps:-

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad \text{initiation}$$

$$\left.\begin{aligned} OH + H_2O_2 &\longrightarrow HOH + HO_2 \\ O_2^- + H_2O_2 &\longrightarrow O_2 + OH^- + OH \end{aligned}\right\} \text{propogation}$$

$$OH + HO_2 \longrightarrow HOH + O_2 \qquad \text{termination}$$

The p_H dependence of the quantum yield favours the assumption that the O_2^- reacts with hydrogen peroxide rather than with the undissociated radical.

The production of oxygen from aqueous solutions of cobaltic ions at room temperature has been explained as due to the formation of OH radicals[26]. An intensive investigation of this subject was carried out by Bawn and White[39,40,41] and the following mechanism suggested

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

$$2OH \longrightarrow H_2O_2$$

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

A method developed by Evans et al[42,43] for the detection of free radicals in solution has been applied to the case of the hydroxyl radical. The method consists in the initiation of polymerisation by the free radical and in the particular instance of Fenton's Reagent

+2 [illegible]

i.e. $Fe^{++} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH$

OH groups have been shown to be present in the polymer chain.

Weiss and his co-workers[44] have examined the effects of X-rays, γ-rays, α particles and neutrons on water and postulated that the primary step is the splitting of the water molecule.

$$H_2O \rightsquigarrow H + OH$$

A number of reviews and discussions have recently been published in this relatively new field of radiation chemistry[45,46,47].

Dainton[48] has demonstrated the production of OH free radicals by the short wave irradiation of water using γ-rays on aqueous solutions of acrylonitrile, resulting in the initiation of chain polymerisation.

(3). Miscellaneous Radicals.

The SH radical has been postulated by Fishgold and Weiss[49]. It is possibly the cause of the cis-trans isomerisation in the system sulphur dioxide, hydrogen sulphide, maleic acid.

A recent suggestion[50] was made that the hydroxyl radical is dissociated in a similar manner to the SH radical

i.e. $OH \rightleftharpoons O^- + H^+$

The N_3 radical was postulated in the reaction

$$Ce^{+4} + N_3^- \longrightarrow Ce^{+3} + N_3$$

The N_3 radical breaks up into nitrogen.

It has been assumed that the NO^- radical ion is produced by electron transfer from NO in solution[22] according to

$$e + NO \longrightarrow NO^-$$

followed by

$$NO^- + H^+ \longrightarrow NOH.$$

B. THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE.

The major pioneering work introducing the concept of inorganic free radicals (OH and HO_2) into the field of reaction kinetics in solution was that of Haber and Weiss[52,53] on the catalytic decomposition of hydrogen peroxide by ferrous and ferric iron.

The proposed scheme was the first complete reaction mechanism based on OH and HO_2 radicals in solution as intermediate entities. Its original form, for the reaction of ferrous iron and hydrogen peroxide, is as follows.

$$\begin{array}{llll}
Fe^{+2} + H_2O_2 & \longrightarrow & Fe^{+3} + OH^- + OH \\
OH + H_2O_2 & \longrightarrow & HO_2 + H_2O \\
HO_2 + H_2O_2 & \longrightarrow & O_2 + H_2O + OH \\
Fe^{+2} + OH & \longrightarrow & Fe^{+3} + OH^-
\end{array}$$

The decomposition is seen to be a chain reaction, with OH and HO_2 radicals as chain carriers, accompanied by oxidation of the ferrous ion.

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

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

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 ion catalysis or a reaction of ferric iron with the HO_2 radical, i.e.

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

would lead to the evolution of oxygen.

Later it was suggested by Weiss[17] 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. Evans, Hush and Uri[19] suggested p_K value of ~ 2 for the ionic dissociation of HO_2 in aqueous solution. Both species HO_2 and O_2^{-} would be present in slightly acid solutions, HO_2 reacting as oxidising agent (the reduction product being HO_2^{-}).

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

and O_2^- reacting as reducing agent (the oxidation product being O_2)

$$O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH.$$

An important modification of the original Haber-Weiss mechanism was put forward almost simultaneously by Barb, e/ Bax~~i~~ndale, George and Hargrave[54], by Weiss and Humphrey[55], and by Medalia and Kolthoff[56]. These authors recognised that the main step leading to oxygen evolution is the reaction

$$Fe^{+3} + O_2^- \longrightarrow Fe^{+2} + O_2$$

This applied not only to the slow decomposition of hydrogen peroxide by ferric ions, where Haber and Weiss have already suggested the reaction

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

but also to the oxygen burst in the reaction of ferrous ion and hydrogen peroxide.

Recently Uri[57] suggested that an important reaction in the Haber-Weiss mechanism had been overlooked viz.

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

This is the reverse reaction of the primary reaction step of the Haber-Weiss scheme. The forward reaction as formulated by Haber and Weiss

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

would indicate termolecular collisions for a back reaction and was consequently not postulated. The formation of an ion-pair complex equilibrium

$$Fe^{+3} + OH^- \rightleftharpoons Fe^{+3}OH^-$$

was not visualised at that time.
The reaction $Ce^{+4}OH^- + OH$ was postulated by Evans and Uri[58] in the photo-oxidation of water by ceric ions.

By including the reaction of $Fe^{3+}OH^-$ with OH radicals in the general reaction scheme for the decomposition of hydrogen peroxide Uri[59] was able to account for the deviation from the kinetic equation at low concentrations of hydrogen peroxide observed experimentally by Andersen[60].

George[61] 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[62] 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[63] 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.

An alternative chain mechanism to that of Haber and Weiss was suggested by Bray and Gorin[64] who assumed the formation of the ferryl ion (tetravalent).

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

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

This mechamism was revived by Medalia and Kolthoff[56], but it was recently pointed out by Uri[65] that this scheme is unlikely.

The formation of ferryl ion by a different mechanism was suggested by Barb, Baxendale, George and Hargrave[66,67]

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

although the authors were not convinced that the experimental evidence for its occurrence is conclusive.

The energetics of the decomposition of hydrogen peroxide are discussed in the review 'The Energetics of Reactions Involving Hydrogen Peroxide, Its Radicals and Its Ions' by Evans, Hush and Uri[19].

C. CHARGE-TRANSFER SPECTRA AND PHOTOCHEMICAL OXIDATION--REDUCTION REACTIONS.

On absorption of visible or ultra-violet radiation by an isolated molecule an electronic transition occurs which may result in a considerable intramolecular redistribution of charge. In the review by Orgel[68] transitions involving intermolecular or inter-ionic charge transfer are discussed. These transitions are in fact photochemical oxidation-reduction reactions and it is from this that their importance in chemistry arises.

The general feature of the spectra is that in the transition responsible for optical absorption an electron, or possibly part of an electron, associated with one molecule or ion is transferred to a different molecule or ion.

Photo-excited electron transfer reactions of inorganic ions in solution are described below.

(1). Anions.

A characteristic feature of the spectra of anions in aqueous solution is the occurrence of a very strong absorption bond in the U.V. about the range 2,000-2,500A°. e.g. the spectra of chloride, bromide and iodide ions show maxima at 1,800 A°., 2,000 A°., 2,300A°., respectively, with molar extinction coefficients in the range 5,000-12,000.

The intense absorption bands of these halide ions were first interpreted as charge transfer spectra by Franck and Scheibe[69]. It was suggested that the absorption of light by a hydrated negative ion was accompanied by formation of a free radical and a hydrated electron. The electron set free by the charge transfer absorption was at first assumed to escape into the bulk of the solvent.

Franck and Haber[21] revised this scheme and postulated the primary process

$$X^-(H_2O) \xrightarrow{h\gamma} H + X + OH^-$$

a/ a/ Fark~~e~~s and Fark~~e~~s[70] pointed out that the primary photochemical process consists of a mere electron transfer from anion to one of the molecules in the hydration layer.

$$X^-(H_2O) \longrightarrow X(H_2O)^-$$

The electron could then return to its original orbit or alternatively some permanent chemical change could take place.

A reaction of the excited molecule $X(H_2O)^-$ with a/ a/

hydrogen ion was postulated by Fark~~e~~s and Fark~~e~~s to account for the dependence of the quantum yield on the hydrogen liberation. In the photo-reduction of water by iodide ions Uri[3] suggests the dissociation

$$I(H_2O)^- \longrightarrow I + H + OH^-$$

the main part of hydrogen liberation being

$$HI + H \longrightarrow I + H_2$$

whilst competing with the secondary dark back reaction

$$H + I \longrightarrow H^+ + I^-$$

The concentration of undissociated hydrogen iodide is dependent on both the iodide and hydrogen ion concentrations.

The spectra of many other ions have been studied with for ultra-violet including OH^-, SH^-, OCl^-, CN^-, ClO_2^-, NO_2^-, ClO_3^-, NO_3^- [71], SO_3^{-2}, SO_4^{-2} [72].

(2). Cations.

Many cations absorb strongly in the U.V. These are attributed to charge transfer processes.

No charge transfer bands have been found for the stable alkali metal ions and alkaline earth metal ions.

The hydrated ions of other metals have been studied by a number of workers particularly Fromberg and his school. The ions studied included Ag^{+}[73], Te^{+}[74], Zn^{++}[75], Cd^{++}[75], Hg^{++}[76], Sn^{++}[77], Pb^{++}[76], V^{++}, Cr^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++}[80].

The nature of the change transfer process responsible for the cation bands is not as obvious as in the case of anions. In suitable circumstances change transfer may be expected either from cation to the solvent or in the opposite direction.

It was suggested by Rabinowitch[81] that in the case of easily oxidised cations the charge transfer absorption of longest wavelength is from the ion to the solvent while in easily reduced cations it is in the opposite direction.

The photo-reduction of water by ferrous ion was observed by Potterhill, Walker and Weiss[78]. The primary process was represented by

$$Fe^{+2}(OH_2) \xrightarrow{h\nu} \underset{\text{excited complex.}}{(Fe^{+2}.OH_2)} \longrightarrow Fe^{+3}(OH_2)^{-} \longrightarrow Fe^{+3} + OH^{-} + H$$

followed by $2H \longrightarrow H_2$

The photo-oxidation of water by ferric iron was reported by Dain and Kachan[82]. The reaction may be written

$$Fe^{+3}.H_2O \xrightarrow{h\nu} Fe^{+2}.H_2O^{+} \longrightarrow Fe^{+2} + H^{+} + OH$$

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

The photochemical formation of hydrogen atoms in aqueous solution was extensively studied by Dainton and James[79]. It was shown that the hydrogen atoms formed by photo-reduction of water, i.e.

$$M^{+n}.H_2O \xrightarrow{h\nu} M^{+(n+1)}.OH^{-} + H$$

initiated the polymerisation of vinyl compounds. Comparison was made by them of the spectra of V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2} and Ni^{+2} which are interpreted as charge transfer spectra. The shift in the absorption maximum towards shorter wavelengths was shown to vary linearly with the increasing ionisation potential of M^{+2} in aqueous solution. The slope of this plot is such that the difference in the absorption maxima translated into energy terms is almost quantitatively the same as the corresponding difference in the ionisation potentials. It thus seems certain that in these ions the charge transfer process is from bivalent ion to the solvent.

(3). Cation-Anion Complexes.

Some cation-anion complexes absorb in the visible or near ultra-violet region and it has been established that the transitions are associated with charge-transfer processes.

The simplest spectra of this type, studied in detail by Fromberg[74], are those of simple binary complexes such as $Pb^{+2}Cl^{-}$;$Pb^{+2}Br^{-}$,$Pb^{+2}I^{-}$. The spectra of these components of solutions of the metal salts were determined by means of the variation of the absorption spectrum with the concentration of the halide ion. The general behaviour agrees well with thet predicted for charge transfer spectra, the maximum occurring at the longest wavelengths for the iodides and shortest for the chlorides.

The most widely studied of the inner complexes of transition metals are those of the ferric ion. Thus a study of the visible spectra of ferric chloride, bromide, and hydroxide Rabinowitch and Stockmeyer[83] succeeded in isolating the spectra of each of the $Fe^{3+}X^{-}$ ions and also those of more complicated ions such as $FeCl_2^{+}$ and $FeCl_3$. The chloride spectra were found to the short wave-length side of those of the bromides in agreement with the work of Fromberg, and the thiocyanate spectrum, measured by Kiss,Abraham and Hegedos[84], was to the longer wave-length side of the bromide.

Rabinowitch[81] postulated that the absorption spectra of ion-pair complexes be interpreted as electron transfer spectra, i.e.

$$M^{n+}X^{-} \longrightarrow M^{(n-1)}X.$$

Evans and Uri[85,86] have shown that in the presence of a polymerisable substrate the free X radicals or atoms formed from ion-pair complexes as a result of a photo-exicted electron transfer process leads to the polymerisation of vinyl compounds. The following ion-pairs were found to act as photo-sensitisers. $Fe^{+3}OH^{-}$, $Fe^{+3}Cl^{-}$, $Fe^{+3}F^{-}$, $Fe^{+3}N_3^{-}$, $Fe^{+3}C_2O_4^{-2}$, $Fe^{+3}HCitr^{-2}$, $Pb^{+2}Cl^{-}$, $Ce^{+4}OH^{-}$.

D. THE PHOTOCHEMISTRY OF FERRIC IRON SOLUTIONS.

It has been known since the middle of last century that photo-reduction of ferric iron takes places in the presence of organic substrates. These were organic acids, e.g. oxalic[87,88,89,90], lactic, mandelic and tartic[91], glycollic[92], citric[93] and pyruvic[94], (in all of which complex formation is likely) and also sugars[95] and a variety of alcohols[96]. In the investigation of the ferric-alcohol system it was suggested that the primary photochemical reaction is the activation of a molecule of ferric chloride, which then reacts with another molecule of ferric chloride, producing ferrous chloride and chlorine, ~~at~~ which directly attacks the alcohols. The reaction was not thought to involve photo-dissociation[97].

The recent rapid achievements on the elucidation of the photochemical properties of ferric salt solutions are due to the postulate by Rabinowitch[81] that the absorption spectra of ion-pair complexes of ferric iron should be interpreted as electron-transfer spectra , the light absorption process being

$$Fe^{+3}X^{-} \xrightarrow{h\gamma} Fe^{+2}X.$$

Arising out of the work of Evans and Baxendale[42,43] on the primary reaction between ferrous ion and hydrogen peroxide

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

it was shown conclusively that this primary reaction involved the formations of a hydroxyl radical and these radicals initiated polymerisation by attacking the double bond of an unsaturated compounds,

$$X + CH_2 = CHR \longrightarrow XCH_2 - CHR -$$

This afforded a sensitive method of detecting the presence of hydroxyl radicals in aqueous solution.

Evans and Uri[85,86] went on to demonstrate the presence of free radicals in irradiated solutions of ion-pair complexes of ferric iron using this technique of iniation of polymerisation. This was the first direct experimental evidence of Rabinowitch's postulate.

The field has developed very quickly since then and it has been shown that atoms or radicals produced photochemically from ion-pair complexes can lead to (a) polymerisation of vinyl compounds, (b) oxidation of organic substrates, (c) photo-oxidation of water. The mechanisms of these reactions are given below.

The energetics of the process

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

have been calculated by Evans and Uri[86]. The energy change ΔE_1 involved in the process is given by

$$\Delta E_1 = -\Delta H_{Fe^{+3}OH^-} + I_{Fe^{+2}} - E_{OH} - S_{OH^-} + S_{OH} + Q_1$$

in which

$\Delta H_{Fe^{+3}OH^-}$ = heat of formation of the ion pair from the separate ions Fe^{+3}(aq) and OH^-(aq.).
$Fe^{+3}(aq.) + OH^-(aq.) = (Fe^{+3}OH^-)aq.$ $\Delta H = -1.2$ kcal.

$I_{Fe^{+2}}$ = ionisation potential of Fe^{+2} in aqueous solution = 97 k.cal.

E_{OH} = electron affinity of OH radical in the gas phase

S_{OH^-} = solvation energy of OH^- ion

$$E_{OH} + S_{OH^-} = 147 \text{ k.cal.}$$

S_{OH} = heat of formation from gas phase of OH radical = 10 k.cal.

Q_1 = energy change required to bring the separate particles $Fe^{+2}(aq)$ and $OH(aq)$ into a configuration identical with that of $Fe^{+3}OH^-$ ion-pair.

w/ ΔE_1 = total energy charge.

The energy change in the process

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

is given by the terms $I_{Fe^{+2}} - E_{OH} - S_{OH} - S_{OH}$ and

$\Delta H = 40$ k.cal.

Substitution of these values in the above equation

$$\Delta E_1 = 90 = -(-1.2) + 40 + Q_1$$

(h)

$\therefore$ Q = 48.8 k.cal.

$\therefore$ approximately 50 k.cal. represents the repulsion energy of compression between Fe^{+2} and OH.

This energy is quite high because the primary transition occurs between $Fe^{+3}OH^-$ and $Fe^{+2}OH$ with no change of interatomic distance (between Fe and O in both complexes), as understood by the Franck-Condon principle , and not between two fully dissociated and solvated states. The energy of compression being considerable one expects the dissociation of $Fe^{+2}OH$ to be a rapid reaction. This was shown from kinetic results later obtained for photo-polymerisation work.

(a) Initiation of Vinyl Polymerisation.

A detailed study was carried out by Evans, Santhappa and Uri[98]. It was unambiguously shown that the ion-pair was the photo-active species from the following.

(a) the rate of ferrous ion formation was a linear function of the light absorption fraction (k_q) due to the ion-pair,

(b) with the species $Fe^{+3}OH^-$, at perchloric acid conc. 1 N and $[Fe(ClO_4)_3] = 10^{-2}\overline{M}$, where the concentration of the ion pair is negligible, the rate of ferrous ion formation and polymerisation was practically nil.

In the case of $Fe^{+3}Cl^-$ and $Fe^{+3}F^-$ the polymers were found to contain Cl and F groups respectively.

The influence of the following factors was studied: light intensity, light absorption fraction due to ion-pair, concentration of vinyl monomer and effect of initially added ferrous ion.

The following mechanism was put forward:

(1) Excitation

$$Fe^{+3}X^- \xrightarrow[k_\varepsilon I]{h\gamma} = Fe^{+2}X$$

(2) Primary Dark Back reaction

$$Fe^{+2}X \xrightarrow{k_d} Fe^{+3}X^-$$

(3) Dissociation of excited complex

$$Fe^{+2}X \xrightarrow{k_s} Fe^{+2} + X$$

(4) Secondary dark back reaction

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

(5) Initiation of polymerisation

$$X + CH_2 = CHR \xrightarrow{k_i} XCH_2 - CHR -$$

(6) propagation of polymerisation

$$X(CH_2CHR)_n- + CH_2 = CHR \xrightarrow{k_p} X(CH_2CHR)-_{(n+1)}$$

(7) Termination

$$X(CH_2CHR)_n- + -(CHRCH_2)_mX \xrightarrow{k_t} X.(CH_2CHR)_{n+m}X.$$

Using stationary state kinetics, the dependence of quantum yield on reaction conditions was found to be

$$\phi = \frac{dFe^{++}\ dt}{k_\varepsilon I} = \frac{k_s}{k_d + k_s} = \frac{k_i[M]}{k_o[Fe^{+2}]+k_i[M]}$$

which was found to be in close agreement with the experimental results.

The following constants were evaluated.

			λ studied
$k_o/k_i \sim 10^3 - 10^4$. $\dfrac{k_s}{k_d + k_s} \sim 5 \times 10^{-2}$	for	$Fe^{3+}OH^-$	313,365 mμ
0.13	"	$Fe^{+3}Cl^-$	313,365 mμ
0.5	"	$Fe^{+3}N_3^-$	313,405 mμ

$\dfrac{kg}{k_d + k_s}$ is the maximum quantum yield.

(b) Oxidation of Organic Substrates.

The effect of light (λ 365 mμ) on the system $Fe^{3+}OH^-$ -benzoic acid was reported by Bates, Evans and Uri[99]. A mechanism was postulated which is in principle similar to that adopted for the initiation of polymerisation reactions, viz.

(1) $Fe^{+3}OH^- \xrightarrow[k\ I]{h\gamma} Fe^{+2}OH$

(2) $Fe^{+2}OH \xrightarrow{k_d} Fe^{+3}OH^-$

(3) $Fe^{+2}OH \xrightarrow{k_s} Fe^{+2} + OH$

(4) $OH + C_6H_5COOH \xrightarrow{k_i} .C_6H_4COOH + HOH$

(5) $OH + .C_6H_4COOH \xrightarrow{k_t} HOC_6H_4COOH$

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

In a later study by Bates and Uri[100] on a number of aromatic substrates it appeared that the formation of salicylic acid by reaction (5) should be replaced by

(a) $Fe^{3+}OH^- + R^\cdot \rightarrow Fe^{+2} + ROH$

except at very low ferric concentration where termination takes place by

(b) $R^\cdot + OH^\cdot \rightarrow ROH$

and (c) $R^\cdot + R^\cdot \rightarrow R_2$.

The photochemical oxidation of benzene in aqueous solution was investigated by Baxandale and Magee[101] with light of 313 mμ.

They found their observations in quantitative agreement with the mechanisms:

$$Fe^{+3}OH^- \xrightarrow{h\gamma} Fe^{+2} + HO$$
$$HO + PhH \rightarrow Ph + HOH$$
$$Ph + Ph \rightarrow Ph_2$$
$$H_2O + Ph + Fe^{+3}(\text{or } Cu^{+2}) \rightarrow PhOH + H^+ + Fe^{+2}(\text{or } Cu^+)$$
$$H_2O + Ph + Fe^{+2} \rightarrow PhH + OH^- + Fe^{+3}.$$

The primary quantum efficiency is 0.13. The relative rates of reaction of the radical Ph with Fe^{+2}, Fe^{+3} and Cu^{+2} are 1, 4 and 30 respectively.

(c) The Photo-Oxidation of Water.

The photo-oxidation of water by ceric ions was studied by Weiss and Porret[102] who assumed the formation of an excited $Ce^{+4\,*}$ ion and oxygen formation would come from

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

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

This photochemical reaction was carefully reinvestigated by Heidt and Smith[103] and they attributed the photochemical activity to ceric dimers. Evans and Uri[58,104] found no evidence of dimerisation and, postulating the ion-pair $Ce^{+4}OH^-$ as the photo-active species, they were able to quantitatively account for Heidt and Smith's results with the following mechanism.

$$\begin{array}{lll}
(1) & Ce^{+4}OH^- \xrightarrow[\lambda\gamma]{k\ I} & Ce^{+3}OH \\
(2) & Ce^{+3}OH \xrightarrow{k_d} & Ce^{+4}OH^- \\
(3) & Ce^{+3}OH \xrightarrow{k_s} & Ce^{+3} + OH \\
(4) & Ce^{+3} + OH \xrightarrow{k_v} & Ce^{+4} + OH^- \\
(5) & Ce^{+4}OH^- + OH \xrightarrow{k_i} & Ce^{+3} + H_2O_2 \\
(6) & 2Ce^{+4}OH^- + H_2O_2 \longrightarrow & 2HOH + 2Ce^{+3} + O_2
\end{array}$$

not rate
determining

However Weiss[105] 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

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

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

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[105]. Using ferric perchlorate solutions they were only 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 with the ceric system Uri[3] considers that in the photo-oxidation of water by ferric iron the two competing reactions would be

$$Fe^{+2} + OH \xrightarrow{k_0} Fe^{+3} + OH^-$$
$$Fe^{+3}OH^- + OH \xrightarrow{k_i} Fe^{+2} + H_2O_2$$

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

Dain and Kachan[82] have measured oxygen evolution from irradiated solutions of ferric perchlorate. Quantum yields of the order of 10^{-3} were found. Some of these results are given in the following table.

TABLE 1. Photochemical Formation of Oxygen by Irradiation of Solutions of Ferric Perchlorate. (According to Dain and Kachan).

NO.	Composition of Solution in Mols./l. $Fe(ClO_4)_3$.	$HClO_4$	Rate of Gas Evolution. (mm³/min.) x 10^2 (N.T.P.).
17	0.33	5.06	5.0
14	0.32	3.0_8	5.2
15	0.32	1.06	5.3
16	0.33	0.10	2.5

The photo-activity is attributed to the hydrated ferric iron $Fe^{+3}(H_2O)_6$.

During the course of recent investigations of polymerisation[86,98] and oxidation of organic substrates[99,100] iniated by the photo-excited ion-pair $Fe^{3+}OH^{-}$, a small amount of photo-reduction was found in the absence of added substrate. This at first indicated photo-oxidation of the water by ferric iron[86]. However, this ferrous formation is now attributed by these workers to oxidisable organic impurities in the distilled water[98,100], presumably because no oxygen was found.

E. THE PRESENT INVESTIGATION.

During the course of a research study on the constitution and photolysis of some ferric ion - organic acid complexes (Miss) M.I. Christie[106] found that ferric ion, in the absence of added substrate, showed a large increase in photo-activity as the pH was raised from 2 to 8. This was incidental to the work at that time and consequently was not pursued.

The photo-reduction of ferric salts in the absence of added substrate has of late been attributed to oxidisable organic impurities in the systems. Some preliminary experiments with ferric chloride solutions ($\sim 10^{-3}\bar{M}$) at the relatively high p_H of 3 indicated to us that the ferrous ion formed on irradiation with U.V. light was rather much if it had to be attributed solely to impurities. Further, concurrent with the high photo-reduction, hydrolysis of the ferric iron to ferric hydroxide was observed to take place.

Previous investigators seem to have confined their researches to iron systems of $p_H < 2$, presumably to avoid the possibility of formation of colloidal ferric hydroxide.

It was therefore decided to investigate the photochemical properties of ferric ion in the absence of added substrate at p_H's > 2 taking into full account the possible heterogenity of these solutions.

Bibliography

1. Steacie, "Atomic and Free Radical Reactions", Reinhold Publishing Corporation, New York (1946).
2. Waters, "The Chemistry of Free Radicals" Oxford University Press, London (1948).
3. Uri, Chem.Rev., 1952, L, 375.
4. Taylor, Z.physik.Chem., 1926, 120, 183.
5. Haber, Naturwiss., 1931, 19, 450.
6. Geib and Hartek, Ber., 1932, 65, 1551.
7. Hinshelwood, Proc.Roy.Soc., 1946, A 188, 1.
8. Lewis and Elbe, J.Chem.Phys., 1942, 10, 366.
9. Eltenton, J.Chem.Phys., 1947, 15, 455.
10. Bates and Saulley, J.A.C.S., 1934, 56, 110.
11. Bodenstein and Schenck, Z.physick.Chem., 1933, B 20,420.
12. Minkoff, Farad.Soc.Disc., 1947, 2, 407.
13. Bayer and Villiger, Ber., 1902, 34, 855.
14, Helms and Klemm, Z.anorg.Chem., 1939, 241, 97.
15 Kassatochkin, Compt.rend.acad.sci., U.S.S.R., 1945, 47, 193.
16. Kassatochkin and Kotov, J.chem.Phys., 1936, 4, 458.
17. Weiss, Trans.Farad.Soc., 1935, 31, 668.
18. Weiss, Trans.Farad.Soc., 1935, 31, 966.
19. Evans, Hush and Uri, Quart. Rev., 1952, 6, 186

20. Taube and Bray, *J.A.C.S.*, 1940, *62*, 3357.
21. Franck and Haber, *Sitzber.preuss.Akad.Wiss.*, 1931, 250.
22. Weiss, *Ann.Repts. on Progress Chem.* (Chem.Society, London), 1947, *44*, 60.
23. Goldfinger and Graf von Schweinitz, *Z.physik.Chem.*, 1933, *B 22*, 241.
24. Haber and Wansbrough-Jones, *Z.physik.Chem.*, 1932, *B 18*, 103.
25. Weiss, *Nature*, 1934, *133*, 648.
26. Weiss, *Naturwiss.*, 1935, *23*, 64.
27. Baxendale and Lewin, *Trans.Farad.Soc.*, 1946, *42*, 126.
28. Evans, *Trans.Farad.Soc.*, 1946, *42*, 101.
29. LuValle and Weissberger, *J.A.C.S.*, 1949, *69*, 1567.
30. LuValle and Weissberger, *J.A.C.S.*, 1947, *69*, 1821.
31. Bonhoeffer and Haber, *Z.physik.Chem.*, 1928, *A.137*, 263.
32. Farkas, Goldfinger and Haber, *Naturwiss.*, 1929, *17*, 674.
33. Bonhoeffer and Reichardt, *Z.physik.Chem.*, 1928, *A.139*, 75.
34. Urey, Dawson and Rice, *J.A.C.S.*, 1929, *51*, 1371.
35. Oldenburg and Reike, *J.Chem.Phys.*, 1938, *6*, 169, 439.
36. Oldenberg and Reike, *J.Chem.Phys.*, 1939, *7*, 487.
37. Kornfield, *Z.physik.Chem.*, 1935, *B.29*, 205.
38. Lea, *Trans.Farad.Soc.*, 1949, *45*, 81.

39. Bawn and White, *J.Chem.Soc.*, 1951, 331.

40. Bawn and White, *J.Chem.Soc.*, 1951, 339.

41. Bawn and White, *J.Chem.Soc.*, 1951, 344.

42. Baxendale, Evans and Park, *Trans.Farad.Soc.*, 1946, *42*, 155.

43. Baxendale, Evans and Kilham, *Trans.Farad.Soc.*, 1946, *42*, 668.

44. Farmer, Stein and Weiss, *J.Chem.Soc.*, 1949, 3241.

45. Burton, *Ann.Rev.Phys.Chem.*, 1950, *1*, 113.

46. Dainton, *Ann.Repts. on Progress Chem.* (Chem. Society London), 1948, *45*, 5.

47. Willard, Ann. Rev. Phys. Chem., 1955, *6*, 141

48. Dainton, *Nature*, 1947, *160*, 268.

49. Fishgold and Weiss, *Nature*, 1936, 137, 71.

50. Weiss, "Symposium on the Mechanism of Electron Transfer Reactions", Societe de Chimie physique, Paris, 1951.

51. Weiss, *Trans.Farad.Soc.*, 1947, *43*, 119.

52. Haber and Weiss, *Proc.Roy.Soc.*, 1934, *A.147*, 332.

53. Haber and Weiss, *Naturwiss*, 1932, *30*, 948.

54. Barb, Baxendale, George and Hargrave, *Nature*, 1949, *163*, 692.

55. Weiss and Humphrey, *Nature*, 1949, *163*, 691.

56. Medalia and Kolthoff, *J.Polym.Sci.*, 1949, *4*, 377.

57. Uri, "L.Farkas Memorial Vol." Research Council of Israel, Speare Publication, No. 1, p. 193.

58. Evans and Uri, Nature, 1950, 166, 602.

59. Uri, Chem.Rev., 1952, L, 383.

60. Andersen, Acta.Chem.Scand., 1948, 2, 1.

61. George, Disc.Faraday Soc., 'The Labile Molecule', 1947, 2, 196.

62. Dainton and Agar, Disc.Farad.Soc., 'The Labile Molecule' 1947, 2, 691.

63. Uri, J.Phys.Coll.Chem., 1949, 53, 1070.

64. Bray and Gorim, J.A.C.S., 1932, 54, 2124.

65. Uri, Discuss.Farad.Soc., 'Heterogeneous Catalysis,1950.

66. Barb, Baxendale, George and Hargrave, Trans.Farad.Soc., 1951, 47, 462.

67. Barb, Baxendale, George and Hargrave, Trans.Farad.Soc., 1951, 47, 591.

68. Orgel, Quarterly Reviews, 1954, 8, 422.

69. Franck and Scheibe, Z.physik.Chem., 1928, A.139, 22.

70. Farkas and Farkas, Trans.Farad.Soc., 1938, 34, 1113.

71. Friedman, J.Chem.Phys., 1953, 21, 319.

72. Ley and Arends, Z.physik.Chem., 1932, B 15, 311.

73. Fromberg and Menschik, Z.physik.Chem., 1929, B 3, 1.

74. Fromberg and Lih, Z.physik.Chem., 1931, A 153, 321.

75. Doehlmann and Fromberg, Z.physik.Chem., 1934, A 171, 353.

76. Fromberg and Lih, 1933, A 167, 103, Z.physik.Chem.

77. Fromberg and Walls, Z.physik.Chem., 1936, A 178, 29.

78. Potteril, Walker and Weiss, Proc.Roy.Soc., 1936, A 156, 561.

79. Dainton and James, Sympos. on Mechanism of Electric Transfer reactions, Paris, 1951.

80. Dainton and co-workers, unpublished data.

81. Rabinowitch, Rev.Mod.Phys., 1942, 14, 112.

82. Dain and Kachan, Doklady Akad.Nauk., S.S.S.R., 1948, 61, 471.

83. Chem.Abs., 1948, 42, 8659.

83. Rabinowitch and Stockmeyer, J.A.C.S., 1942, 64, 335.

84. Kiss, Abraham and Hegedus, Z.anorg.Chem., 1940,244,98.

85. Evans and Uri, Nature, 1949, 164, 404.

86. Evans and Uri, J.Soc.Dyers Colourists, 1949,65, 709.

87. Draper, Phil.Mag., 1857, 14, 161.

88. Allmand and Webb, J.Chem.Soc., 1929, 1518.

89. Allmand and Webb, J.Chem.Soc., 1931, 3079.

90. Livingston, J.Phys.Chem., 1940, 44, 601.

91. Ghosh and Purkayastha, J.Indian.Chem.Soc., 1929, 6,827.

92. Baur, Z.Electrochem., 1919, 25, 102.

93. Burt, J.Am.Pharm.Assoc., 1928, 17, 650.

94. Lipmann, Skand.Arch.Physiol., 1937, 76, 186.

95. Ross, J.A.C.S., 1906, 28, 790.

96. Presad and Limayl, J.Indian.Chem.Soc., 1933, 10, 91 and 101.

97. Presad, Mohite and Niqudkar, J.Univ.Bombay, 1936, A 156, 561.

98. Evans, Santhappa and Uri, J.Polym.Sci., 1951, 7, 243.

99. Bates, Evans and Uri, Nature, 1950, 166, 869.

100. Bates and Uri, J.A.C.S., 1953, 2, 2754.

101. Baxendale and Magee, Trans.Farad.Soc., 1955, 51, 205.

102. Weiss and Porret, Nature, 1937, 119, 1019.

103. Heidt and Smith, J.A.C.S., 1948, 70, 2476.

104. Evans and Uri, Symposium No. 5, 'Carbon dioxide Fixatives and photosynthesis' Soc. for Exp.Biology, Sheffield 1950, p. 130. Camb.University Press, (1951).

105. Weiss, ibid., p. 143.

106. Christie, Ph.D. Thesis, Glasgow, 1949.

PART I.

THE PHOTOCHEMICAL REDUCTION OF FERRIC CHLORIDE SOLUTIONS.

Introduction.

The effect of organic impurities in the distilled water as a complicating factor in kinetic investigations was postulated by Kolthoff ane Medalia[1] in their study of oxidation reactions with Fenton's Reagent. The system ferrous ion hydrogen peroxide ethanol was studied in detail in the presence and in the absence of oxygen. The stoichiometric overall reaction for the decomposition of hydrogen peroxide is

$$2\ Fe^{+2} + H_2O_2 + 2\ H^+ \rightarrow 2Fe^{+3} + 2\ H_2O$$

when ferrous ion is greatly in excess, i.e. the stoichiometric ratio $R = \frac{\text{moles of } Fe^{+2} \text{ reacted}}{\text{moles of } H_2O_2 \text{ reacted}} = 2.$ Deviations from the stoichiometric ratio are found in the reaction between hydrogen peroxide and ferrous ion in the presence of various organic substances (due to the competing reactions $Fe^{+2} + OH$, and substrate + OH) and the investigation of Kolthoff and Medalia[1] deals with a study of these deviations. However, it was found that in the absence of added organic substrate, when the concentrations of the primary reactants were small (10^{-3}M and less), the reaction

---

[1] Kolthoff and Medalia, J.A.C.S., 1949, 71, 3777, 3784.

ratios greatly differed from 2. This was at first attributed to small amounts of organic impurities in the reagents. Systematic investigations showed that the induced reaction could be almost eliminated by distillation of the water from alkaline permanganate. Further it was shown that 'impure' water gave similar results to these found with 'pure' water in the presence of small amounts of various organic compounds. It was then concluded that the deviation from stoichiometric results must be attributed to the traces of organic impurities in the water.

Simultaneously and independently the significance of these impurities was discovered by Barb, Baxendale, George and Hargrave[2] in a study of the oxidation of leuco dyes to dyes by Fenton's reagent. While Kolthoff and Medalia worked with concentrations of $[H_2O_2]$ and $[Fe^{+2}]$ of the order of 10^{-3}M, this investigation was carried out under conditions in which the concentration of reactants was about 100 times smaller. Consumption ratios of Fe^{+2}/H_2O_2 up to 4 were obtained in the presence of oxygen without addition of any substrate. It is suggested that this be attributed to traces of organic impurities.

---

[2] Barb, Baxendale, George and Hargrave, Trans.Farad.Soc., 1951, 47, 462.

Evans and Uri[3] found that in ferric perchlorate solutions irradiated in the absence of an added substrate there is an accumulation of ferrous ion and suggested that it is due to the removal of OH radicals by the reaction.

$$OH + OH \rightarrow H_2O + O$$

after the initial dissociation of the ion-pair

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

The overall reaction would be the photo-oxidation of water.

Barb[4] proposed that the accumulation of Fe^{+2} observed by Evans and Uri was due to the attack of OH radicals on organic impurities in the distilled water:-

$$OH + RH \rightarrow R + H_2O$$
$$R + Fe^{3+}OH^- \rightarrow ROH + Fe^{+2}$$

Later work of Evans and Uri[5] and Bates and Uri[6] provides evidence that the possibility of organic impurities in distilled water water cannot be ignored. For example, in the investigation of Evans and Uri on the photo-oxidation of water by ceric ion the following mechanism is pro-

---

[3] Evans and Uri, J.Soc.Dyers and Colourists, 1949, 65, 709.

[4] Barb, Ph.D. Thesis, Leeds

[5] Evans and Uri, ~~Photochem. Workers Polym. , Ce^{+4}OH$^-$~~ Nature, 1950, 166, 602.

[6] Bates and Uri, J.A.C.S., 1953, 2754.

posed:-

$$
\begin{array}{rcl}
Ce^{+4}OH^- & \xrightarrow[h\nu]{k\ I} & Ce^{+3}OH \\
Ce^{+3}OH & \xrightarrow{k_d} & Ce^{+4}OH^- \\
Ce^{+3}OH & \xrightarrow{k_s} & Ce^{+3} + OH \\
Ce^{+3} + OH & \xrightarrow{k_o} & Ce^{+4} + OH^- \\
Ce^{+4}OH^- + OH & \xrightarrow{k_i} & Ce^{+3} + H_2O_2 \\
2Ce^{+4}OH^- + H_2O_2 & \longrightarrow & 2HOH + 2Ce^{+3} + O_2
\end{array}
$$

not rate
determining

Stationary state kinetics leads to the following expression for the quantum yield.

$$\gamma_{Net} = \frac{dCe^{+3}\ \ dt}{k\ I} = 4.\frac{k_s}{k_d+k_s} \cdot \frac{k_i[Ce^{+4}OH^-]}{k_o[Ce^{+3}] + k_i[Ce^{+4}OH^-]}$$

The maximum quantum yield is $4.\frac{k_s}{k_d+k_s} = 0.2$. It was stated that when impurities in the distilled water compete with $Ce^{+4}OH^-$ for the OH radical (at low ceric concentrations) the maximum yield found was, in accordance with expectations,

$$\frac{k_s}{k_d+k_s} = 5 \times 10^{-2}$$

In a study of the oxidation of aromatic compounds by photo-excitation of ferric ion-pairs Bates and Uri[6] showed that the dependence of ferrous ion formation on the ferric ion concentration in the absence of any substrate was similar to that in the presence of substrate. This, together with the fact that they found this photochemical reduction of ferric iron in the absence of added substrate "*without accompanying oxygen evolution*" was strong evidence for the postulations of organic impurities.

The photochemical oxidation of benzene in aqueous solution by ferric iron was recently reported by Baxendale and Magee[7]. In a careful investigation they were able to analyse the products of the reaction quantitatively. Assuming ferrous ion, phenol and diphenyl to be the only products there should be an oxidation balance

$$2[Fe^{2+}] = [PhOH] + [Ph_2]$$

to the accuracy of the analytical methods which were estimated as ± 5%. However, throughout the work a consistent discrepancy in this oxidation-reduction balance was found, in that twice ~~half~~ the amount of Fe^{+2} was always about 10% in excess of the organic products. Light intensity, ferric ion, benzene and acid concentrations were all varied without observing any marked change although the amounts and composition of the products varied considerably. Oxidisable impurities were suspected which, however, seemed

---

[7] Baxendale and Magee, *Trans.Farad.Soc.*,1955,*51*,205.

unlikely for three reasons.

(a) Redistillation of the water from alkaline permanganate before use had no effect.

(b) The oxidation of such impurities would compete with the oxidation of benzene so that if the same entity (OH) was responsible for both, the discrepancy would increase as the benzene concentration decreased. This was not observed.

(c) The same source of water was used in the Fenton oxidation of benzene[8] where good oxidation belances were invariably obtained.

It was also observed by Baxendale and Magee that some reduction of Fe^{+3} takes place in the nominal absence of oxidisable substrates. They report that whether this is the oxidation of organic matter still present or whether it is an oxidation of water is difficult to decide. In the latter case oxygen or hydrogen peroxide would be expected. Hydrogen peroxide was ruled out since no change in $[Fe^{+2}]$ was observed when the solution was left standing after irradiation. It is suggested that a formation of oxygen in the benzene system cannot be through some reaction like

---

[8] Baxendale and Magee, Faraday Soc.Disc., 1953, 14, 160.

$HO + OH \rightarrow H_2O + \frac{1}{2}O_2$.

as any reaction of OH must compete with the reaction of OH with benzene. So the lack of oxidation balance cannot be explained by photo-oxidation of water. They were unable to account for the discrepancy.

In all these photochemical investigations considerable effort was made to purify the distilled water free from alleged impurities, but to no avail. Indeed it was shown by Fricke and Hart[9,10] some time ago, in a radio-chemical investigation, that traces of organic impurities in distilled water could be quantitatively removed only by irradiation with X-rays.

In the present work preliminary experiments showed that our irradiation of a $10^{-3}\bar{M}$ ferric chloride solution, pH3, at 20°C., ferrous ion was produced to the extent of $3.9 \times 10^{-4}\bar{M}$, i.e. a photo-reduction of 30%. This was considered to be rather high if due solely to oxidisable organic impurities in the distilled water and it was decided that an attempt should be made to obtain conclusive experimental evidence as to the effect, if any, of these alleged impurities.

---

[9] Fricke and Hart, J.Chem.Phys., 1936, 4, 418.

[10] Fricke and Hart, J.Chem.Phys., 1938, 6, 229.

The photochemical reaction was therefore studied under different conditions of temperature, p_H, age of solution etc.,and in the presence of added organic and inorganic substrates.

Since a thorough kinetic study was not invisaged at this stage an apparatus which was considered to give the required results with greater speed was preferred to an orthodox photochemical arrangement.

Experimental.

Materials. The water used for the preparation of solutions was purified by distillation using a variety of methods.

(a) An all-glass Pyrex still.

(b) A Bousefield Conductivity Water Still[1] (copper boiler and block tin fractionation dome and condenser).

(c) Water treated with alkaline permanganate and distilled in a Pyrex still.

(d) Distillation of previously strongly irradiated iron solutions followed, a number of times, by addition of more ferric chloride to the distillate, re-irradiation and redistillation (iron solutions $1.3 \times 10^{-3}\bar{M}$, p_H 3.05).

The condensers and receivers were sterilised with steam before collection of the water.

Since it was later found that the solutions prepared from these different preliminary treatments all gave agreeing

---

[1] Bousefield, J.Chem.Soc., 1912, 101, 1443.

[2] Goodwin, Z.Physik.Chem., 1896, 21, 1.

[3] Goodwin and Grover, Phys.Rev.,[1], 1900, 11, 195.

[4] Lamb and Jacques, J.A.C.S., 1938, 60, 967, 1215.

photo-reductions, water distilled in Pyrex glassware was henceforth used.

All other chemicals were of A.R. Grade unless otherwise stated.

Iron Stock Solution.

Earlier workers investigating hydrolysis phenomena in iron solutions, prepared by dilution of a concentrated stock solutions, 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[4] prepared their dilute solutions by the addition of a small weighed portion of the anhydrous salt to pure water.

An irreproducibility with regard to photo-sensitivity has been found in this work when the solutions were prepared from a concentrated iron stock solution. A method, however, which was found to give entirely satisfactory reproducibility in the photo-reduction 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., was pipetted with an 'Agla' micrometer syringe (supplied by Burroughs Wellcome Co.) into a measured quantity of water. When not in use the stock was allowed to resolidify.

Preparation of Solutions.

Solutions 1.3 x 10^{-3}M in ferric iron were prepared by adding 0.1 ml. A.R. $FeCl_3.6H_2O$ liquid melt dropwise from the syringe with constant stirring into 500 ml. of distilled water. This solution had a p_H of 3.05. For lower p_H values the ferric chloride was added to an appropriately dilute solution of hydrochloric or perchloric acid. Stock solutions of the acids were prepared from the A.R. materials.

When it was desired to have a 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 rate of stirring was found to have an effect on the experimental results at higher p_H's a standard procedure was adhered to throughout.

Analysis.

The percentage reduction was determined by estimation of ferric iron before and after irradiation with titanous chloride solution, using ammonium thiocyanate as an indicator, the titration being done under carbon dioxide. With the micro-burette used, titres on the same solution were reproducible to within ± 0.2%.

Direct analysis of ferrous ion colorimetrically with the ferric-dipyridyl complex[5] was made in a number of instances to confirm the trustworthiness of the titanous chloride method.

Likewise an occasional determination of Ferrous ion by potassium permanganate (using 'Zimmerman and Reinhardt's solution since Cl^- present) was carried out as an additional check.

Agreeing results were obtained in every case.

-p_H Determination.

The hydrogen ion concentration was measured with a glass electrode and the usual valve electrometric circuit. The standard buffers used were 0.05M potassium hydrogen phthalate (p_H 4.00) and 0.05M borax (p_H 9.18).

Measurement of Secondary Hydrolysis.

On dilution of an iron salt with water "primary" hydrolysis produces all the species:-

$$Fe^{+++} \overset{HOH}{\rightleftharpoons} \underset{\substack{+\\H^+}}{Fe(OH)^{++}} \overset{HOH}{\rightleftharpoons} \underset{\substack{+\\H^+}}{Fe(OH)_2{}^{+}} \overset{HOH}{\rightleftharpoons} \underset{\substack{\text{(in sol-}\\\text{ution)}}}{Fe(OH)_3} \rightleftharpoons \underset{\substack{\text{(coll-}\\\text{oidal)}}}{Fe(OH)_3}$$

the concentrations of the species being dependent on p_H, temperature and total concentration of ferric iron[4].

By participation of the anion of the iron salt used other complexes will also be possible in greater or lesser amounts. In the present system there will probably be present species such as $FeCl^{++}$, $Fe(OH)Cl^{++}$...[5]. In recent work it is claimed that the direct $Fe_2(OH)_4^{4+}$ as well as $Fe(OH)^{++}$ is present in solution[6].

Sooner or later, depending on the p_H, iron concentration and temperature, this primary hydrolytic equilibrium breaks down, moving to the right with the gradual formation of colloidal ferric hydroxide. The process of secondary hydrolysis is probably to be ascribed to the breaking down of the metastable supersaturated concentration of ferric hydroxide in solution[4]. All the solutions investigated were initially colourless. The onset and development of this "secondary" hydrolysis, accompanied as it is by the formation, due to ferric hydroxide[4], of

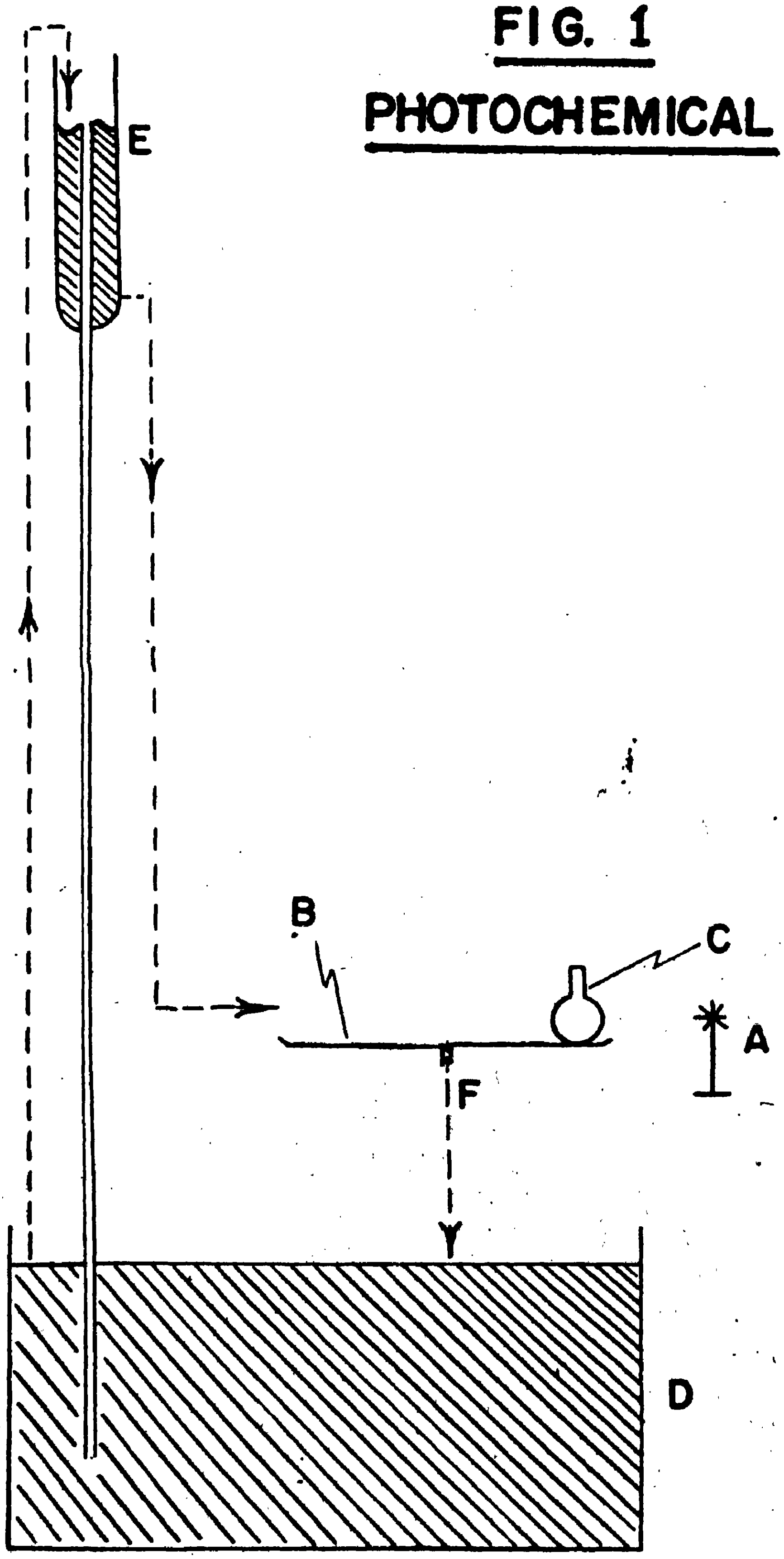
---

[5] Rabinowitch and Stockmeyer, *J.A.C.S.*, 1942, *69*, 335.

[6] Hedström, *Arkiv-Chemi.*, 1953, *6*, 1.

FIG. 1

PHOTOCHEMICAL APPARATUS



a reddish-brown colour, was followed by the increase in optical density with time using a Hilger 'Spekker' Absorptiometer and Ilford 601 filters (peak transmission 4250 A°.).

Irradiation Apparatus.

A diagramatic representation of the apparatus is shown in Fig. 1.

The light source, A, unfiltered, was a 500 Watt Hanovia mercury arc lamp (Type S,500). A stainless-steel table, B, of diameter 45 cm., was constructed to hold round its circumference ten quartz flasks, C, each 300 ml. capacity and fitted with a B.34 Quickfit neck. On this table each flask had a 'seat' made of three rubber sucker plugs, all flasks being gauged 4 cm. from the lamp. The table was turned at a uniform speed of 4 r.p.m. by an electric motor through a reduction gear, each flask thus receiving the same light dosage.

To maintain the flasks at a steady temperature (temperature has a profound influence on the hydrolytic equilibrium[4]) water was pumped from a large thermostat bath, D, up to a constant head E, from which a tapping was taken to six small nozzles, situated round the table in such a way that the rotating flasks were continuously hosed during a run with the constant temperature water. All jets faced the oncoming flasks so that leaving one flask the jet immediately fell onto the next, assuring an efficient use of the cooling water. The water was drained from the table via its hollow driving shaft, F, and returned to the bath below. In order that the quartz surface of the flasks were readily wetted, a little detergent, lissapol N.D.B., was added to the thermostat water. Using this arrangement the solutions could be kept at T°C. ± 0.1°C., when T was varied between 10°C. and 40°C. Room temperature variation of ± 3°C., did not significantly affect the efficiency of the temperature control.

The flasks were 'charged' in two ways; one by filling to the top and inserting B.34. Quickfit stoppers so that no air bubbles were left; the other by adding only

200 ml. of solution to the flasks and evacuating the air space through a vacuum tap fitted to a B.34 cone. Both ways gave agreeing results and the former was consequently adopted.

Reduction-time curves were determined by taking flasks off the table at noted time intervals and estimating the ferric iron left. The effect of added substrates was measured by having different Ferric/substrate ratios in each flask and irradiating for a fixed exposure time, with subsequent analysis of the iron and in some cases the substrate products.

Results.

(A). Stock Solutions.

An $\bar{M}/10$ stock solution was prepared from A.R. ferric chloride and solutions of $1.3 \times 10^{-3}\bar{M}$ by dilution of this stock. They had a'natural' p_H of 3.05 due to hydrolysis. On exposure for 2½ hours at 20°C., during which secondary hydrolysis took place, a photo-reduction of 18.5% was attained. However, 11 days later a $1.3 \times 10^{-3}\bar{M}$ solution prepared from the same stock and with the same exposure at 20°C. achieved only a 14.5% reduction. That this phenomenon was due only to the ageing of the solution was shown by preparation of a fresh $\bar{M}$ 10 stock which gave an 18.5% reduction as before. It was thought that this effect was due to some hydrolysis of the stock solution and it was decided to prepare a more concentrated solution of higher acidity.

A stock solution of 0.32 $\bar{M}$ ferric chloride of p_H=0 was prepared from the A.R. salt. This solution gave reproducible values, showing no ageing effect. However, the photo-reduction values of a fresh stock, prepared to the above specifications, differed appreciably from the first stock, although they were consistent in themselves. Measurements of Goodwin and Grover[3] on the hydrolysis of ferric iron differed greatly in most instances from the earlier ones of Goodwin[2]. They suggest that the differences may have been due to the different 'stock' solutions from which the dilute solutions, whose hydrolysis was studied, were prepared.

It will be noted that a correlation between photo-reduction and hydrolysis is becoming apparent.

Moore[7] and Michel[8] concluded that the rate of iron hydrolysis was extremely sensitive to minute differences in the method by which the dilute solutions were prepared.

The A.R. Ferric chloride which was used in the present work has the advantages of both a stock solution, easy dilution of the melt, and a solid salt - no ageing effect in the resolidified melt. The results were reproducible using salt from different sources. In view of Moore and Michels' work, together with our own experience of the reproducibility of the photo-reduction, a standard dilution procedure was adhered to.

---

[7] Moore, Phys.Rev., 1901, 12, 164.

[8] Michel, Compt.Rend., 1907, 147, 288.

(B). Photo-Reduction as a Function of p_H and Temperature.

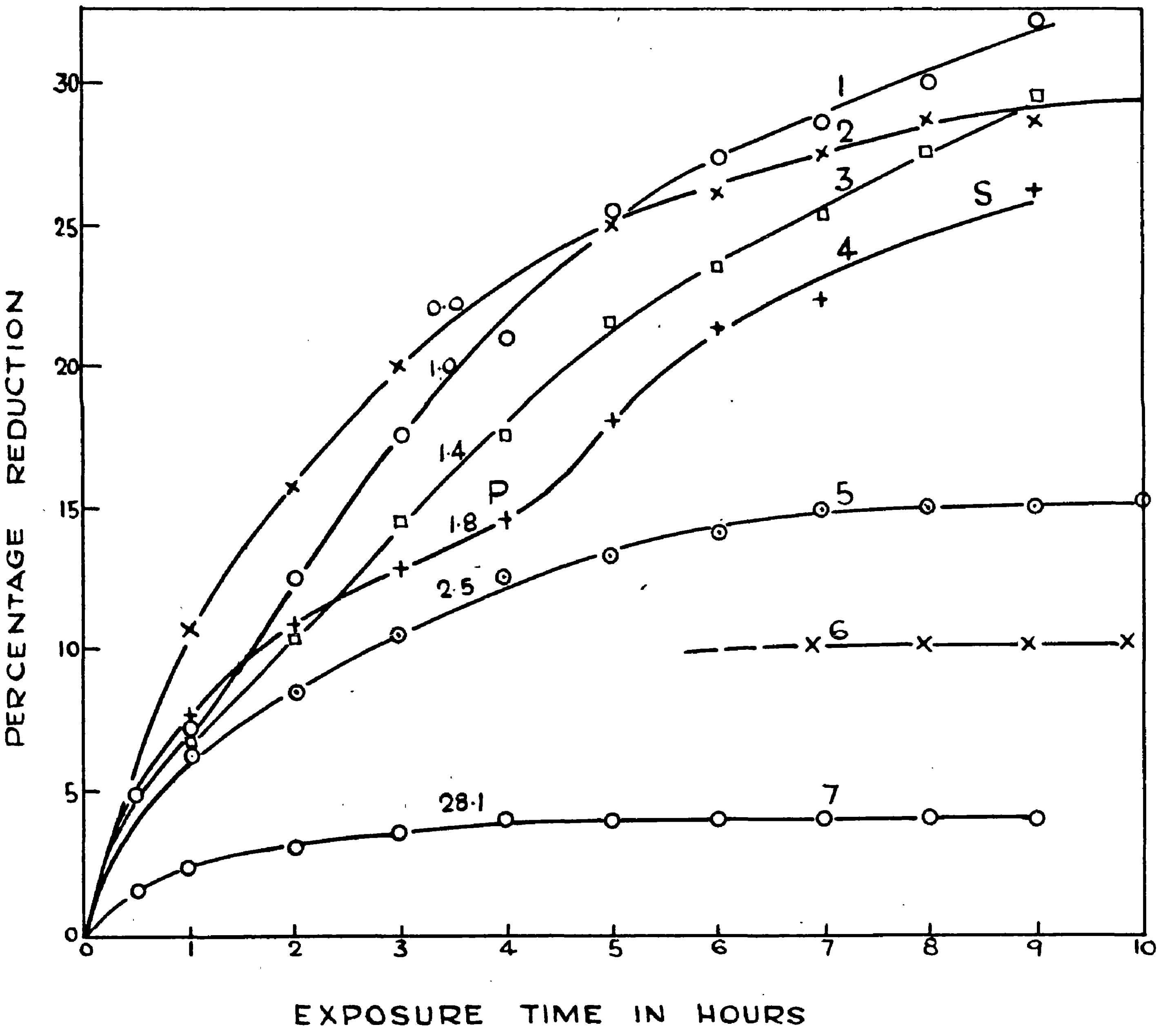
A $1.3 \times 10^{-3}\bar{M}$ ferric chloride solution had a p_H of 3.05. The formation of colloidal ferric hydroxide took place within 90 minutes in the dark at 20°C. For lower p_H values the salt was added to an appropriately dilute solution of hydrochloric or perchloric acid (Table 2).

$\bar{M}$ of Acid Solution x 10^4	p_H of Iron Solution	
0	3.05	1.
4	2.94	2.
5.6	2.92	3
7.2	2.89	4
10.0	2.85	5.
20.0	2.70	6.
40.0	2.49	not shown
112.4	2.05	7

Table 2.

The effect of p_H on photo-reduction at 20°C. is shown in Fig. 2. The system is markedly p_H dependent in this range studied. It is seen that the rate of

FIG. 2. VARIATION OF EXTENT OF REDUCTION WITH DURATION OF EXPOSURE FOR DIFFERENT INITIAL pH's

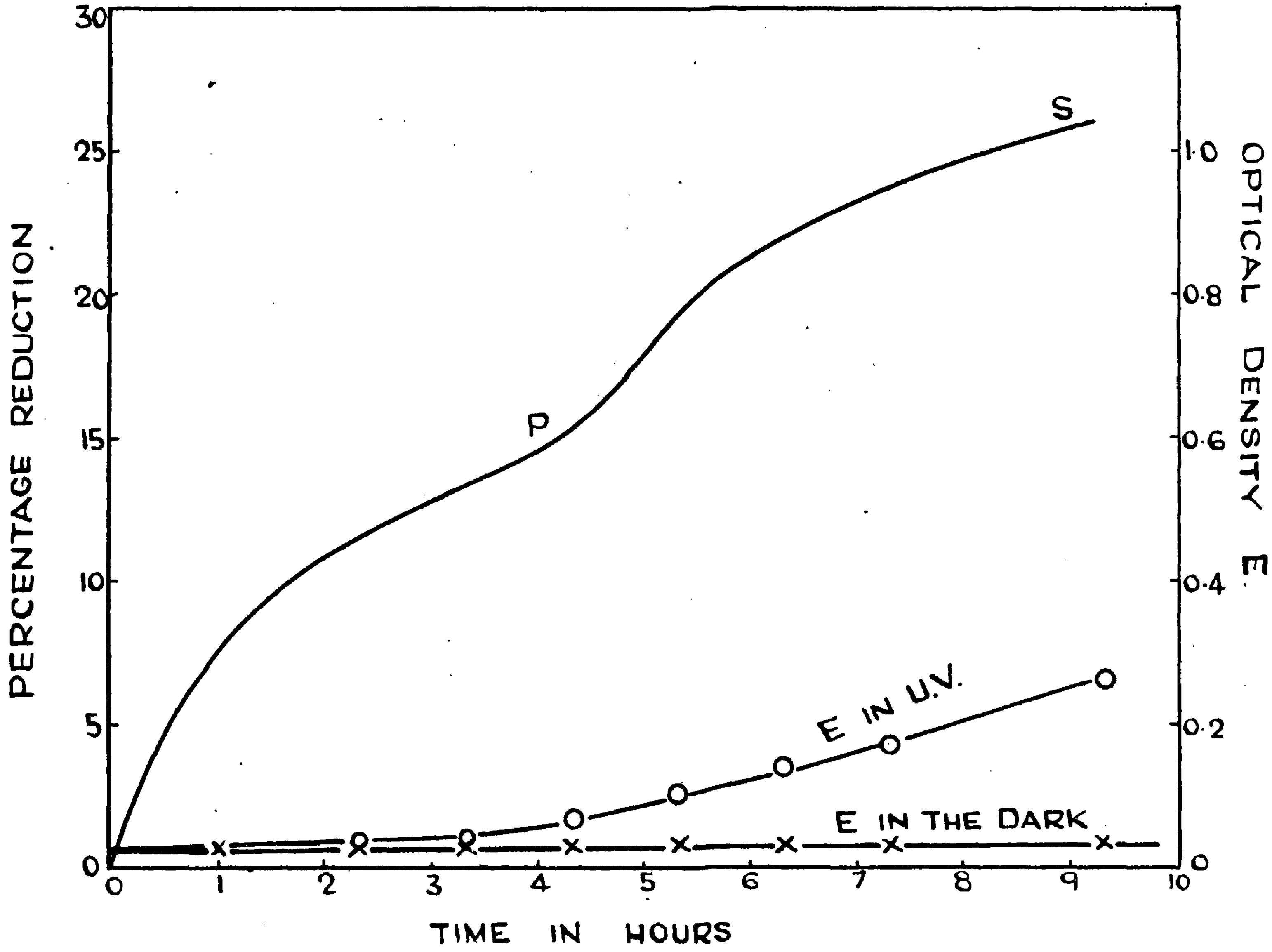


ferrous iron formation decreases with time, the system tending to reach a stationary state especially at the lower p_H's.

At p_H 2.05 the reduction reached a stationary value of 1.53×10^{-5} moles Fe^{++} and at p_H 3.05 a maximum value of 1.15×10^{-4} moles Fe^{++} was achieved with the exposure given.

Secondary hydrolysis took place early in the exposure at the high p_H whereas the more acid one remained colourless. The appearance of secondary hydrolysis, it will be remembered, is indicated by the production of the reddish-brown ferric hydroxide (page 51). In order to assess the effect of the hydrolysis on the photo-reduction the following procedure was adopted. The secondary hydrolysis was followed in conjunction with the reduction values by measuring the optical density of each solution, as it was removed from the table, for iron analysis, on a Hilger "Spekker" using 4 cm. cells and Ilford 601 filters. By trial the iron solution was acidified to delay the secondary hydrolysis until about half-way through the 10 hr. exposure (the lower the p_H the longer the induction period prior to hydrolysis[4]). This was achieved at p_H 2.89

FIG. 3. SHOWING THAT THE BOOST IN PHOTO-ACTIVITY CO-INCIDES WITH THE ONSET OF SECONDARY HYDROLYSIS



seen as curve OPS in Fig. 2. From O to P the reduction rate falls off relatively quickly as compared with p_H 3.05. At P secondary hydrolysis begins and there is quite a sudden increase in the rate of ferrous ion formation PS, i.e. the appearance of colloidal ferric hydroxide increases the photo-activity of the solution. A comparison of the variation of optical density of the solution in this region of 4,000–4,500 Å . (Ilford 601 Filters) with that of photo-reduction, both as a function of time, is shown in Fig. 3. At higher p_H values secondary hydrolysis sets in earlier and the portions OP and PS in Fig. 2 soon merge. At lower p_H values the appearance of secondary hydrolysis is delayed.

At this stage another phenomenom became evident, that of the acceleration of secondary hydrolysis by light. In Fig. 4 curves show a comparison of change of optical density (4,000–4,510 Å .) with time of two portions of the same $1.3 \times 10^{-3}\bar{M}$ iron solution of p_H 3.05 at 20°C., one kept in the dark while the other was exposed to U.V. light. A similar comparison is given by curves 2 for the iron solution of p_H 2.89. This influence of light on hydrolysis was found to be closely associated with

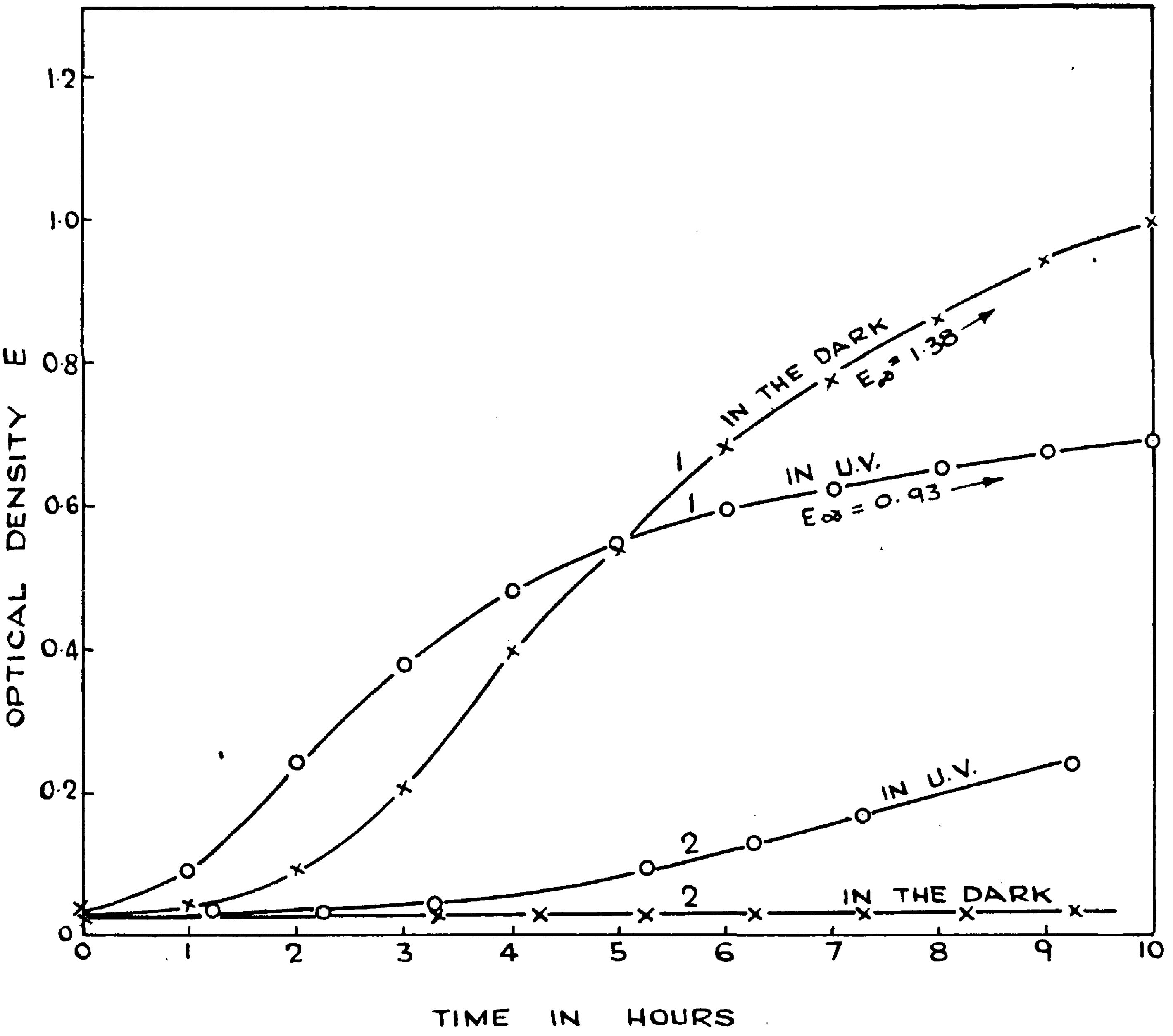


FIG 4. VARIATION OF OPTICAL DENSITY, E, WITH TIME IN THE DARK AND IN THE LIGHT.

CURVES 1, pH 3·05
CURVES 2, pH 2·89

photo-reduction of the iron and will be described in more detail in Part 5 of this thesis.

The lower the temperature the longer is the induction period prior to the onset of secondary hydrolysis[4]. To confirm that the appearance of ferric hydroxide solution was responsible for an increased yield of ferrous iron the reduction rate of a $1.3 \times 10^{-3}\bar{M}$ ferric chloride solution of initial p_H 3.05 was measured at different temperatures (Fig. 5) and an effect similar to p_H variation was obtained. At 12°C. measurements of the optical density of the solution showed that secondary hydrolysis sets in at about P. The influence of temperature on a solution of low p_H (2.05) which showed no visible signs of hydrolysis is shown in Fig. 7 the stationary amount of Fe^{++} is seen to be increased by increase in temperature.

(C). The Stationary State.

It is seen from the previous section that the photo-reduction tends to reach a stationary value with time, the stationary concentration of Fe^{++} increasing with increase of p_H.

Estimation of the photo-produced ferrous iron

FIG. 5. EFFECT OF TEMPERATURE ON THE REDUCTION - TIME CURVE AT pH 3·05.

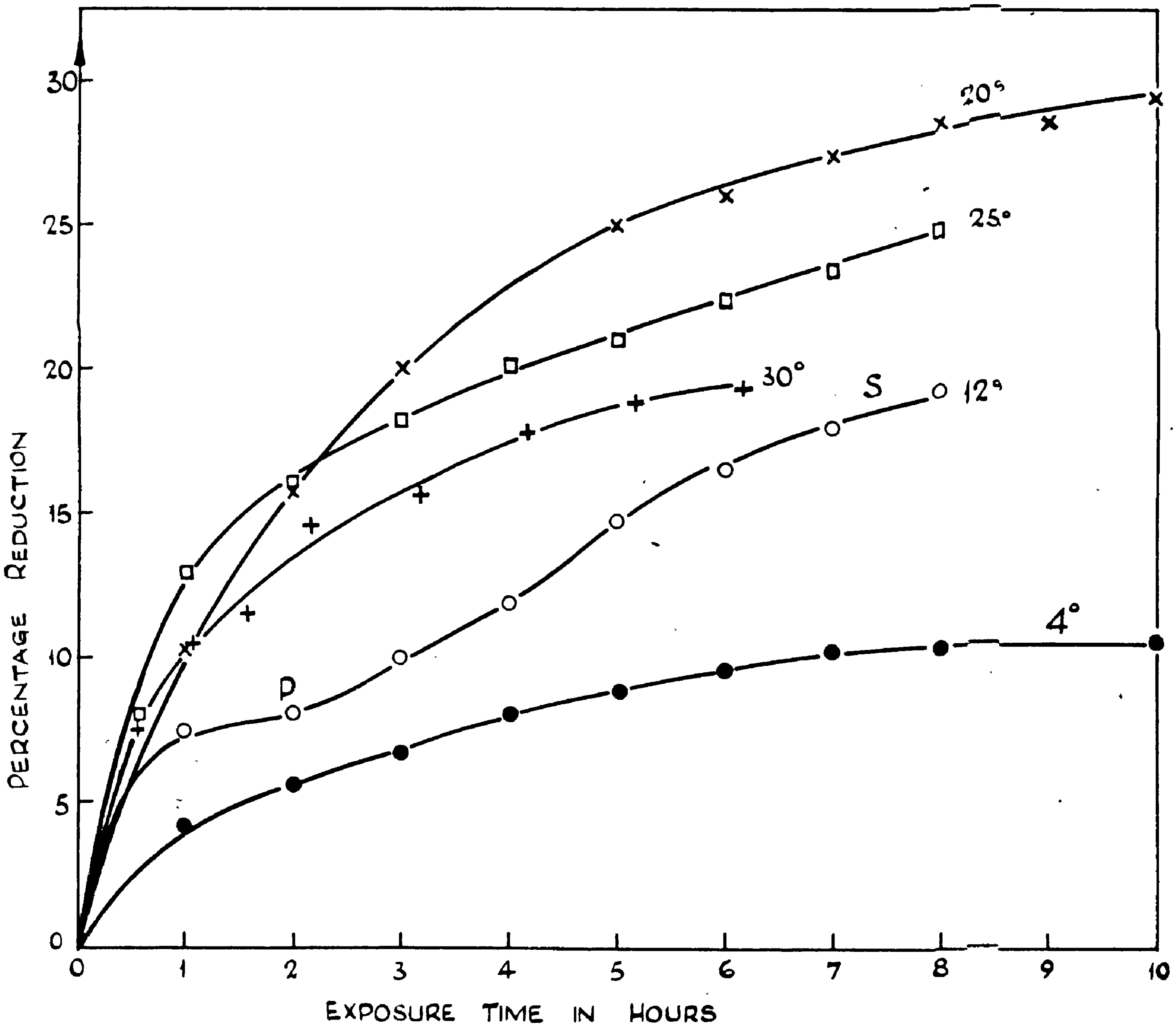
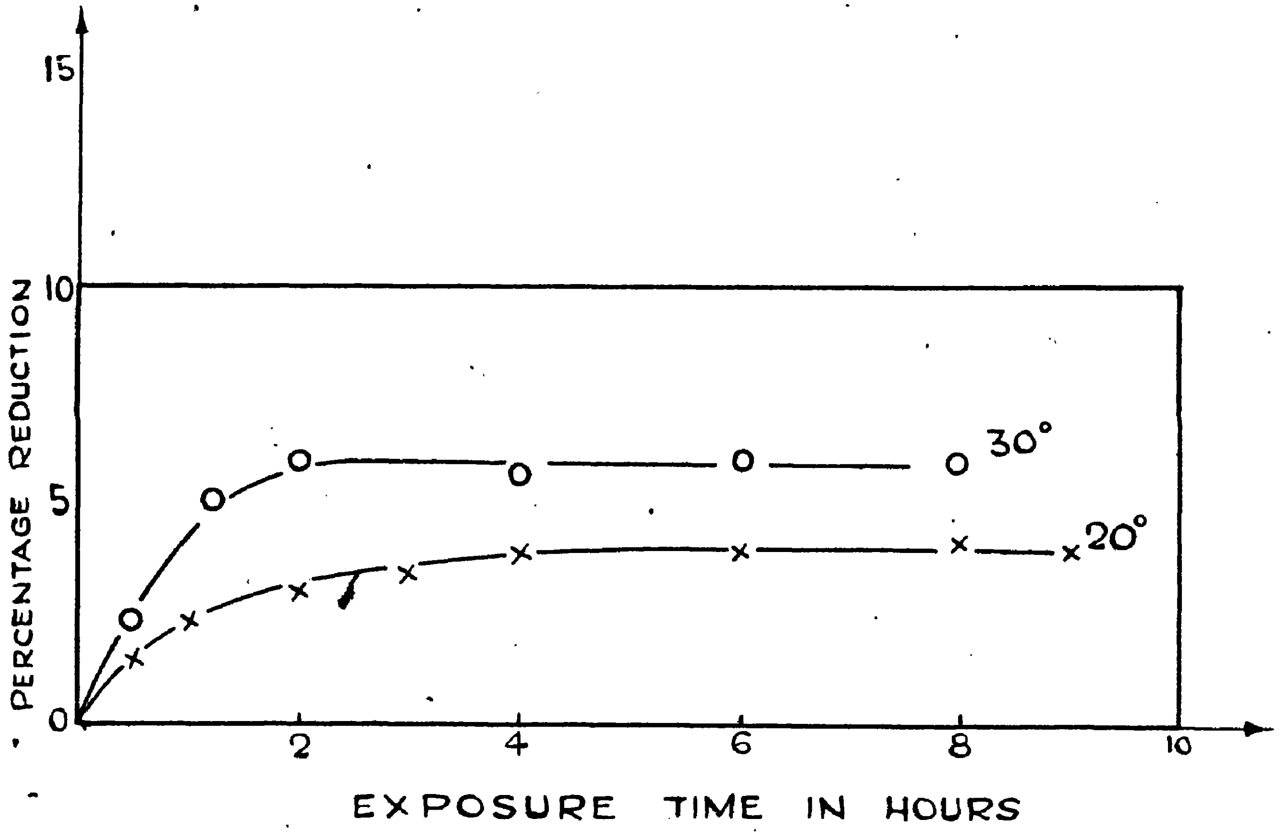


FIG. 7 EFFECT OF TEMPERATURE ON THE REDUCTION-TIME CURVE AT pH 2·05



(colorimetrically) immediately after irradiation and 72 hours later showed no change indicating the absence of a post-irradiation reaction.

Dainton[10] has shown a photo-equilibrium between ferrous and ferric iron to exist in the case of irradiation of solutions of ferrous iron with 2537 Å. light in the presence of acrylonitrile, and represents the equilibrium by the equations,

$$Fe^{2+}H_2O \xrightarrow{h\gamma} Fe^{3+}OH^- + H$$

$$Fe^{2+} + OH \xleftarrow{h\gamma}$$

the net result being the photo-sensitised dissociation of water into hydrogen atoms and hydroxyl radicals, the free radicals being consumed in the polymerisation of the acrylonitrile.

In the present system where a stationary state is reached starting with ferric iron, any photochemical back-oxidation of Fe^{++} must be negligible as may be expected from a comparison of extinction coefficients of ferric and ferrous ions over the spectrum used[11].

---

[10] Dainton, "The Kinetics and Mechanisms of Inorganic Reactions in Solution", Chemical Society Special Publication, No. 1, p. 18.

[11] Potterhill, Walker and Weiss, Proc.Roy.Soc., 1936, Series A, 156, 561.

The ferrous ion absorbs only a very small fraction of the light. This was verified experimentally by exposing a $1.3 \times 10^{-3}\bar{M}$ ferric chloride solution of p_H 2.85, at 20°C., until a stationary state of 5.75×10^{-5} moles Fe^{++} was achieved (no secondary hydrolysis). By the addition of a small amount of concentrated HCl solution the p_H was made < 2. On reirradiation for the same exposure time the stationary value remained unchanged. If a true photo-stationary state existed the stationary concentration of ferrous iron should have fallen to one appropriate to the lower p_H.

Thus it follows that in this system the equilibrium is due to

$$[\text{Ferric}] \underset{\text{Dark}}{\overset{\text{U.V.}}{\rightleftharpoons}} [\text{Ferrous}]$$

By the iniation of polymerisation of vinyl compounds it has been shown that the species $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ are photo-sensitive[12,13].

Since chloride is the anion used in the present

---

[12] Evans and Uri, Nature, 1949, 164, 404.

[13] Evans, Santhappa and Uri, J.Polym.Science, 1951, 7,243.

investigations, and since the p_H range dealt with (2.0-3.0) is indicative of advanced primary hydrolysis, both of these species will be present although the p_H dependence of the photo-reduction points to a hydroxyl complex as the photo-active one in this system. A later analysis of their respective absorption fractions shows this to be very likely.

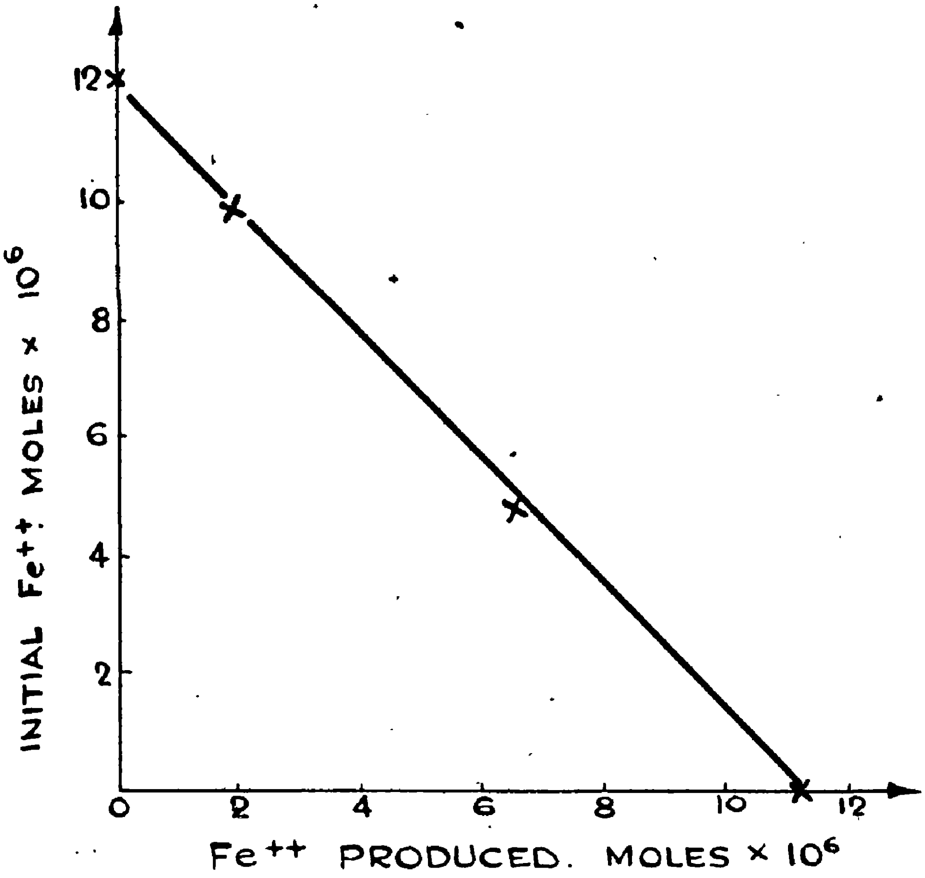
A general reaction covering these possibilities would be

$$[\text{Ferric Complex}] \underset{\text{Dark.}}{\overset{\text{U.V.}}{\rightleftharpoons}} Fe^{+2} + X(OH \text{ or } Cl)$$

i.e. the thermal back reaction is the oxidation of ferrous iron by a free radical.

The effect of initially added ferrous may be understood on this basis shown in Fig. 8. The $1.3 \times 10^{-3}\bar{M}$ ferric solution used was of p_H 2.80. The temperature was kept at 20°C. and solutions with the various Ferric Ferrous ratios were each given an exposure of 6 hours, ample for the attainment of the stationary value. Secondary hydrolysis did not take place under the conditions of these experiments. It is seen that with initially added Fe^{++} not exceeding the stationary state

FIG. 8.



12
10
8
6
4
2
0
2
4
6
8
10
12
INITIAL Fe++: MOLES × 10^6
Fe++ PRODUCED. MOLES × 10^6

value expected for that p_H, then

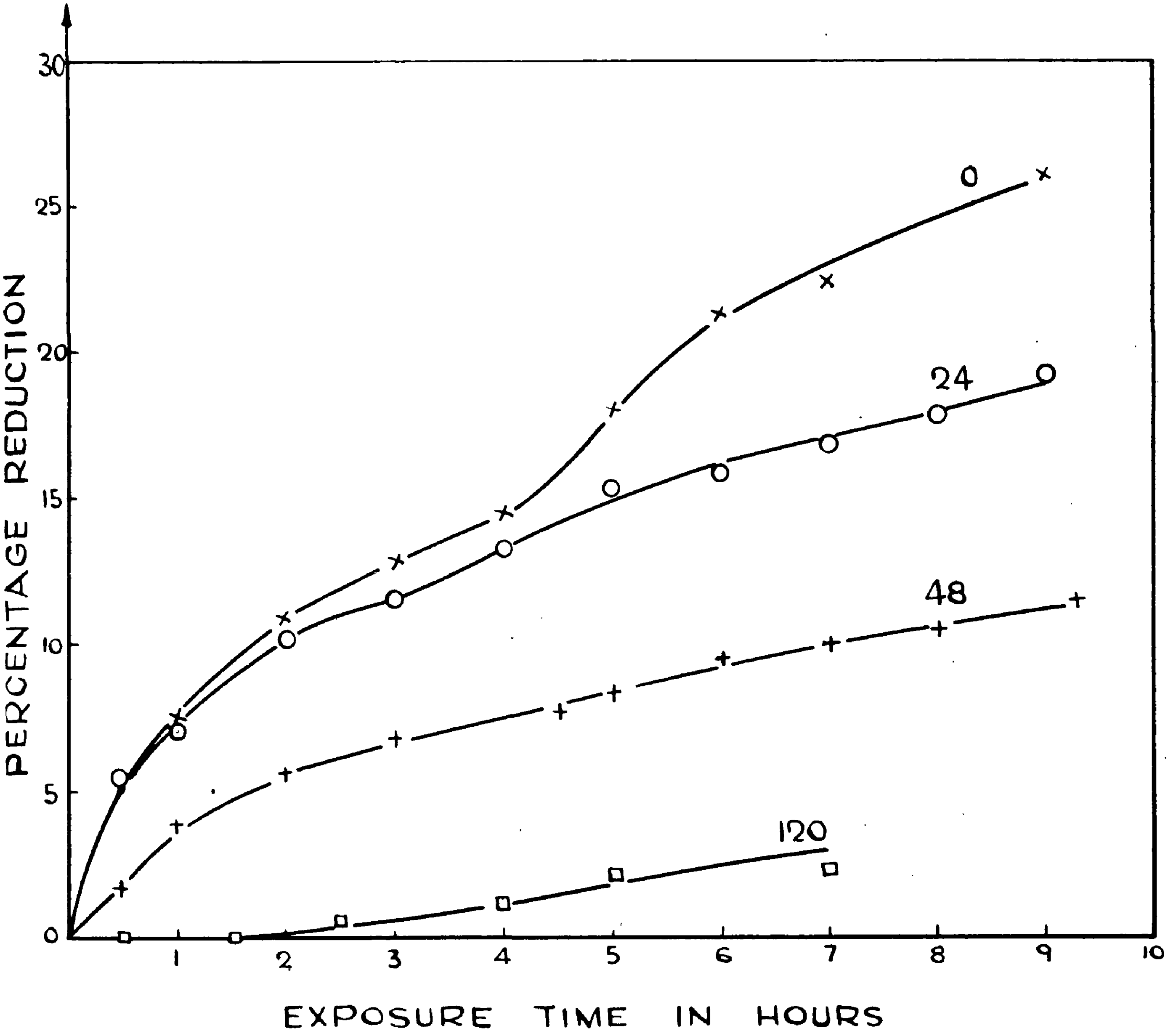
$$[Fe^{+2}]_{initial} + [Fe^{+2}]_{products} = \text{constant} = \text{stationary state conc.}$$

When Fe^{+2} is added initially in such amount as to be the stationary photo-produced ferrous ion for that p_H, no more ferrous is produced.

A stationary state of 3.83×10^{-5} moles of Fe^{+2} was measured at p_H 2.45. Back oxidation of this photochemically produced Fe^{+2} by the addition of a small excess of hydrogen peroxide ('Laporte's' A.R. material, without stabiliser) and reirradiation of the system after a period of standing gave the same stationary Fe^{+2} concentration as before. Before the solution was reirradiated the complete back oxidation of the photo-produced Fe^{+2} by the added H_2O_2 was confirmed by analysis with the ferric--dipyridyl complex[5]. That no H_2O_2 remained after standing was tested by means of the H_2O_2 pertitanic acid colour reaction (yellow).

Three repetitions of this alternate exposure and oxidation on the same solution produced in no instance any significant difference in the yield of Fe^{+2}. These experiments were carried out on solutions whose p_H was such that secondary hydrolysis had not begun at their conclusion.

FIG 9. EFFECT OF AGE ON THE PHOTO-REDUCIBILITY OF 0·0013 M $FeCl_3$ SOLUTIONS, pH 2·89. THE NUMBERS ON THE CURVE INDICATE THE AGE OF THE SOLUTIONS IN HOURS BEFORE EXPOSURE



(D). Ageing.

The effect of ageing the diluted iron solution in the dark was investigated at a low and high p_H.

At p_H 2.2 a 1.3 x $10^{-3}\overline{M}$ ferric chloride solution was aged at 20°C. Reduction/Time curves for this ageing solution taken every second day over a period of three weeks gave no indication of a change in photo-activity. Secondary hydrolysis did not take place within this time.

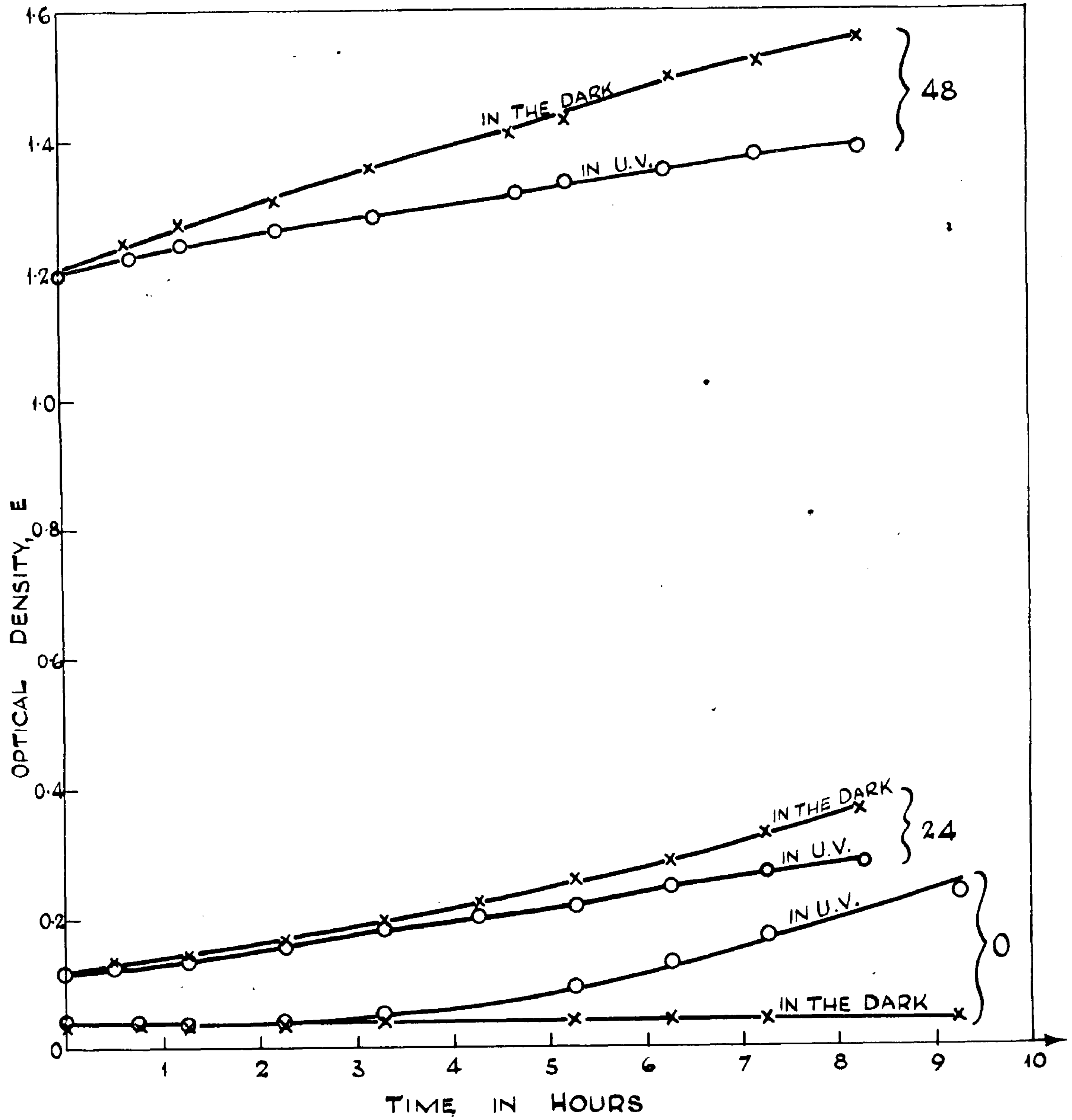
However, a 1.3 x $10^{-3}\overline{M}$ solution of p_H 2.89 in which secondary hydrolysis begins in 4 hours at 20°C. when exposed to U.V. light, (in contrast to an induction period of approximately 15 hours in the dark) showed a very marked decrease in photo-activity with age (Fig.9), i.e. when colloidal ferric hydroxide became the predominant species. The course of the secondary hydrolysis for this ageing solution is shown in Fig. 10.

A qualitative comparison of particle size of ferric hydroxide solutions, by means of the 'Tyndall Effect', between the two solutions,

A. p_H2.89, age 0, hydrolysis initiated by U.V. exposure,

and B. p_H2.89, age 24 hrs. hydrolysis begun in the dark. showed that while a very marked 'Tyndal ' cone was ex-

FIG. 10. INFLUENCE OF LIGHT ON THE HYDROLYSIS OF SOLUTIONS (pH 2·89) OF DIFFERENT AGES. THE NUMBERS AT THE BRACES INDICATE THE AGE IN HOURS.



hibited by B, solution A, although brown in colour, was almost clear. It can be inferred that the particle size in solution A $\ll$ than in B. This is readily understood since solution A has hydrolysed much faster (U.V. curve in Fig. 10). It follows that the colloidal surface available in A $\gg$ than in B for the same hydrolytic conversion. This may explain why the 'heterogenic' effect (namely, the boost in photo-reduction on the appearance of secondary hydrolysis), is found in A but not in B.

(E). The Effect of Organic Substrates.

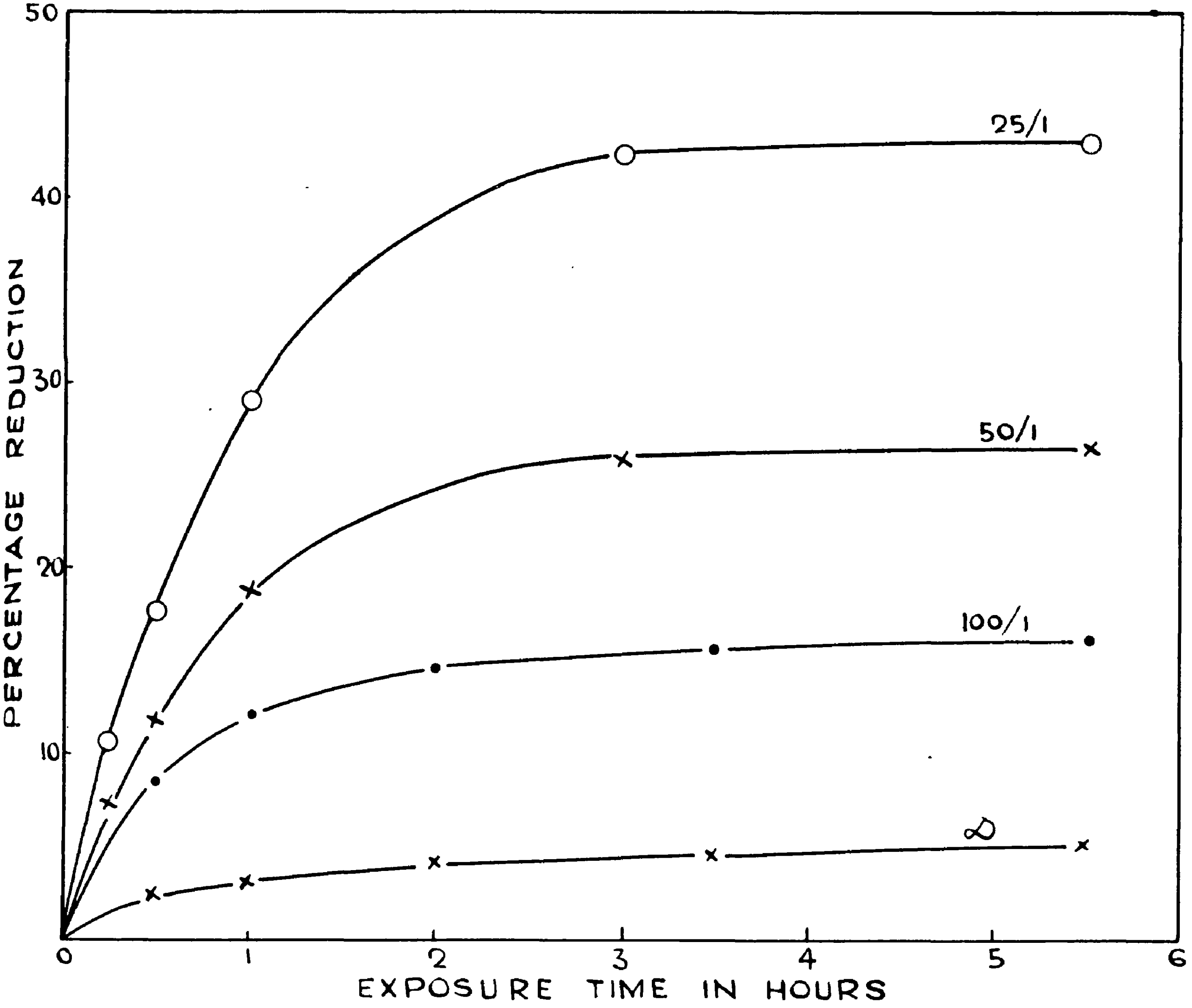
Three substrates were investigated, glucose, benzoic acid and benzene.

(i). Glucose. The A.R. material was used. At the iron glucose concentrations investigated complex formation was considered to be negligible.

Reduction time curves for 1.3 x 10^{-3}M Fe^{+3} showing the effect of glucose concentration at 20°C. and p_H2.45 are shown in Fig. 11. Secondary hydrolysis did not take place.

It is seen that the higher the substrate concentration the higher is the stationary concentration of Fe^{+2}.

FIG. 11. REDUCTION-TIME CURVES AT pH 2·45 IN THE PRESENCE OF GLUCOSE. THE NUMBERS INDICATE THE RATIO $[Fe^{+++}] / [GLUCOSE]$



This is due of course to the competing reactions.

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

$$\text{Glucose} + X \longrightarrow \text{Products.}$$

No attempt was made to analyse the reaction products from the Glucose. This experiment showed that stationary conditions were reached in 3 hours. Thus the effect of substrate concentration at different p_H's was determined by exposing the iron glucose solutions for 5 hrs.

From Fig. 12 it can be seen that there is a constant difference in Fe^{+2} produced with the 3 p_H values independent of substrate concentration and that this same difference is shown experimentally to exist in the absence of added substrate. This result is discussed later.

(ii) Benzoic Acid. The system was $10^{-3}\overline{M}$ Fe^{+3}, $3 \times 10^{-3}\overline{M}$ Benzoic acid. After 5 hr. irradiation no Fe^{+3} was left and this aqueous solution gave a characteristic red colour with added ferric chloride showing the presence of salicylic acid. (The solution temporarily turned red during the exposure).

This photo-oxidation of benzoic acid to salicyclic acid by ferric iron was first reported by Bates, Evans and Uri[14]. Using ferric perchlorate solutions it is

---

[14] Bates, Evans and Uri, 1950, Nature, 166, 869.

FIG. 12. EFFECT OF GLUCOSE ON THE PERCENTAGE REDUCTION. THE NUMBERS INDICATE THE pH VAL

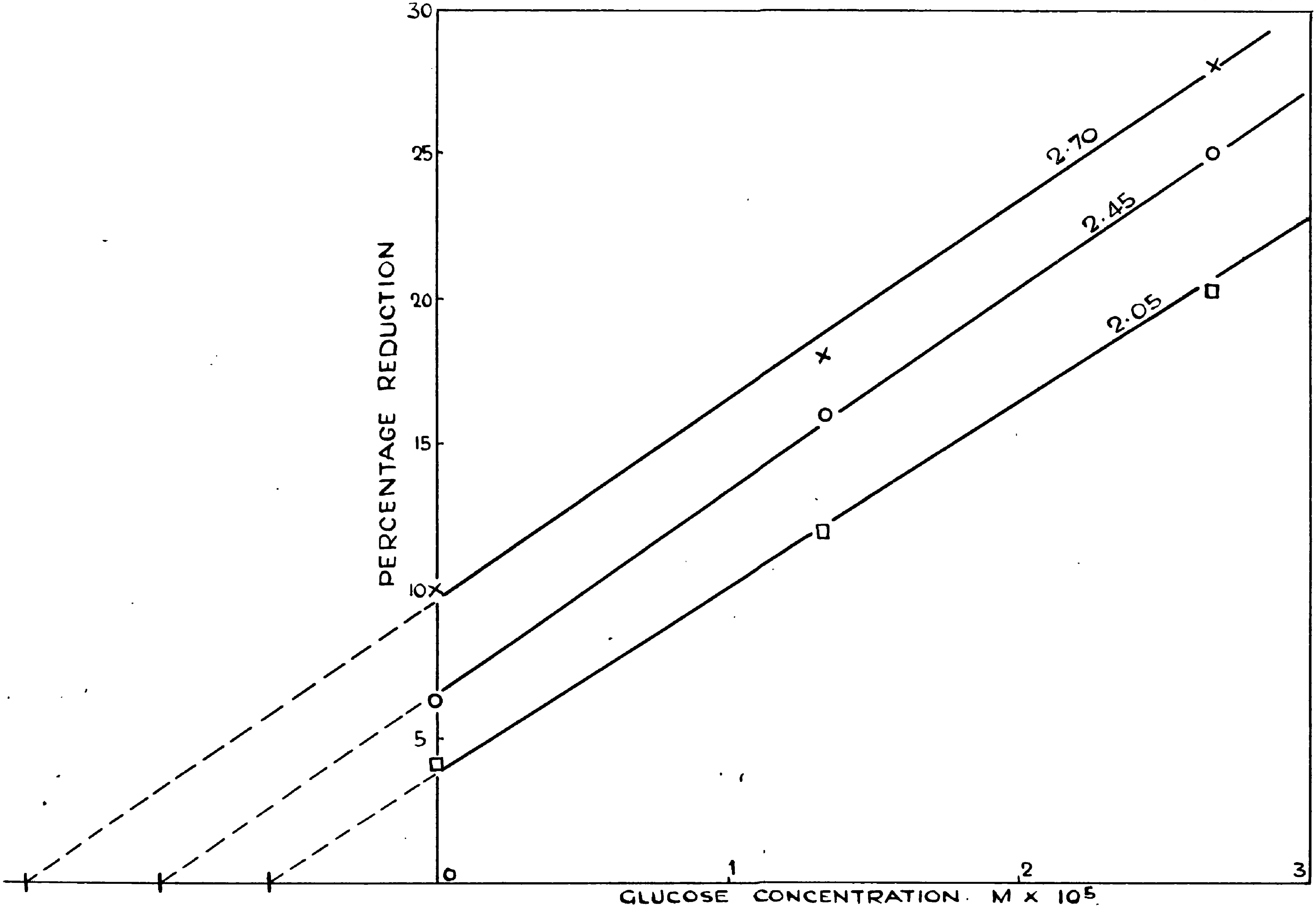
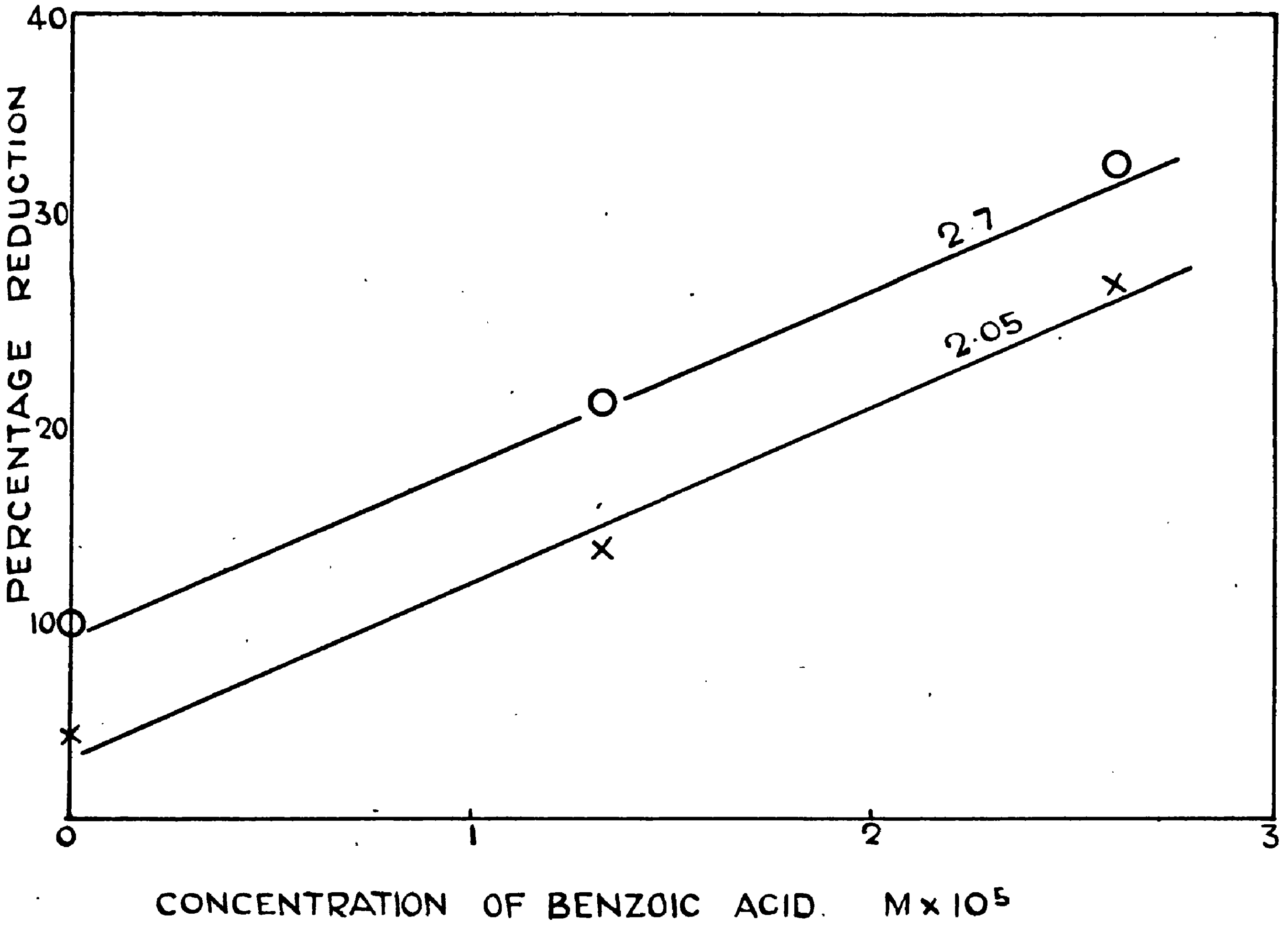
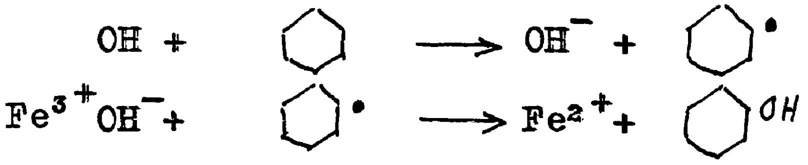


FIG. 13. EFFECT OF BENZOIC ACID ON THE PERCENTAGE REDUCTION. THE NUMBERS INDICATE THE pH VALUES.



suggested that the OH radical attack on the benzene nucleus results after the dissociation of the complex $Fe^{3+}OH^{-} \xrightarrow{h\nu} Fe^{+2} + OH$. The effect of substrate concentration at different p_{H}'s is shown in Fig. 13. This is a similar result to that of the iron glucose system. Secondary hydrolysis did not take place.

(iii). Benzene. The photo-oxidation of benzene by ferric iron was recently investigated by Baxendale and Magee[15]. They found phenol and diphenyl as the only products. Their mechanism is similar to that of Bates, Evans and Uri for benzoic acid except that the effect of ferric iron on the kinetics showed the phenol to be produced by



and not

The system used here was 1.3 x $10^{-3}\bar{M}$ Fe^{+3} saturated aqueous solution of benzene (approximately 0.15% at room temperature). The water used for the solution was freed from oxygen by bubbling nitrogen through it and,

---

[15] Baxendale and Magee, Trans. Far. Soc., 1955, 51, 205.

without excessive precautions, the solution was kept oxygen free as far as possible until transferred to the irradiation vessel.

After five hours irradiation the iron was found to be completely reduced. The solution was acidified with dilute sulphuric acid and then extracted with ether. The ether was extracted with NaOH, Na_2CO_3 and $NaHCO_3$. This gave four fractions including the non-acidic fraction after the alkali extractions.

The Na_2CO_3 and $NaHCO_3$ fractions gave no residue.

The presence of phenolic species in the NaOH fraction was determined with the diazonium compound Naphthalene sulphonic acid-4-nitro-1-diazobenzene[16] by the usual phenol-diazonium salt coupling reaction. This stable solid diazonium compound used was prepared by Mr. C. Stewart in this laboratory for the colorimetric determination of small quantities of pure phenol[17].

The NaOH extract was neutralised with hydrochloric acid and to 10 ml. of this solution, 4 ml. of a 100 mg. per cent solution of the diazonium salt in 0.1 $\overline{M}$ HCl was

---

[16] Heinrich and Schuler, Helv.Chim.Acta., 1947, 30, 886.

[17] Stewart, B.Sc. Thesis, Glasgow, 1953.

added followed by 2 ml. of a saturated solution of sodium acetate. The resulting solution was allowed to stand in the dark for 90 minutes at the end of which 2 ml. of 2 $\bar{M}$ NaOH was added. The deep yellow-red colour formed indicated the presence of phenolic species. Pure phenol of concentration $10^{-4}\bar{M}$ gave a similar colour.

From the non-acidic fraction a small waxy residue was isolated. The presence of diphenyl was indicated by a faint blue colour-reaction with $AlCl_3$[18].

It may be concluded from these experiments with benzoic acid and benzene that an OH radical is produced in the ferric chloride - U.V. system in the p_H range investigated and a later discussion shows this to come direct from a photo-active hydroxyl complex and not through some thermal reaction by a chorine atom.

(F). The Effect of Some Inorganic Anions.

The main purpose of this section was to examine the effect of added Cl^- on the photo-reaction since chloride was the iron salt used. The anions perchlorate, sulphate and phosphate were also studied.

---

[18] Stein + Weiss, J. Chem. Soc., 1949, 3245.

The materials used, sodium chloride, sodium sulphate and sodium hydrogen phosphate, were of A.R. Grade. A neutral sodium perchlorate stock solution (0.65 $\bar{M}$) was prepared from sodium hydroxide and A.R. perchloric acid.

The concentration of ferric chloride was 1.3 x $10^{-3}\bar{M}$ throughout while the substrate concentration was varied from 10^{-5} to $10^{-1}\bar{M}$. A fixed exposure time of $3\frac{1}{2}$ hours was adhered to.

Fig. 14 shows the moles of Fe^{++} formed with variation of concentration of sulphate and phosphate at two p_H's, 2.95, 2.35.

3/ 4/ Tables ~~2~~ and ~~3~~ indicate the appearance of the solution before and after irradiation at p_H 2.95.

TABLE 3.

$\bar{M}$ of SO_4.			10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
Appearance of iron solution-. ($1.3x10^{-3}M$)	(a)	before exposure	faint brown clear	brown clear.	green-brown slightly colloidal.	green-brown colloidal	green-brown colloidal
	(b)	after exposure	brown clear	brown clear	precip. out.	precip. out.	precip. out.

FIG. 14. EFFECT OF SO_4'', PO_4'' ON PERCENTAGE REDUCTION

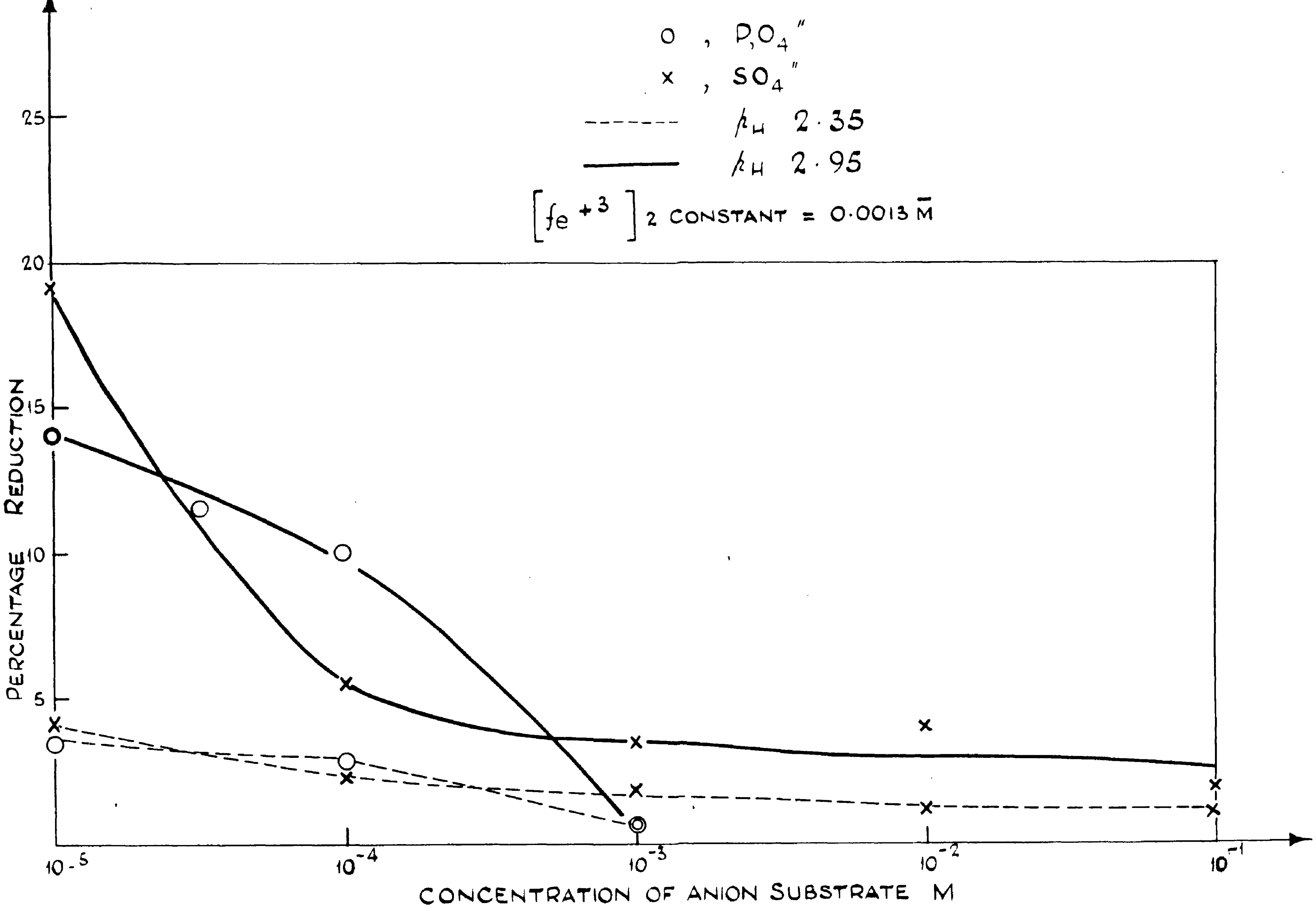


TABLE 4.

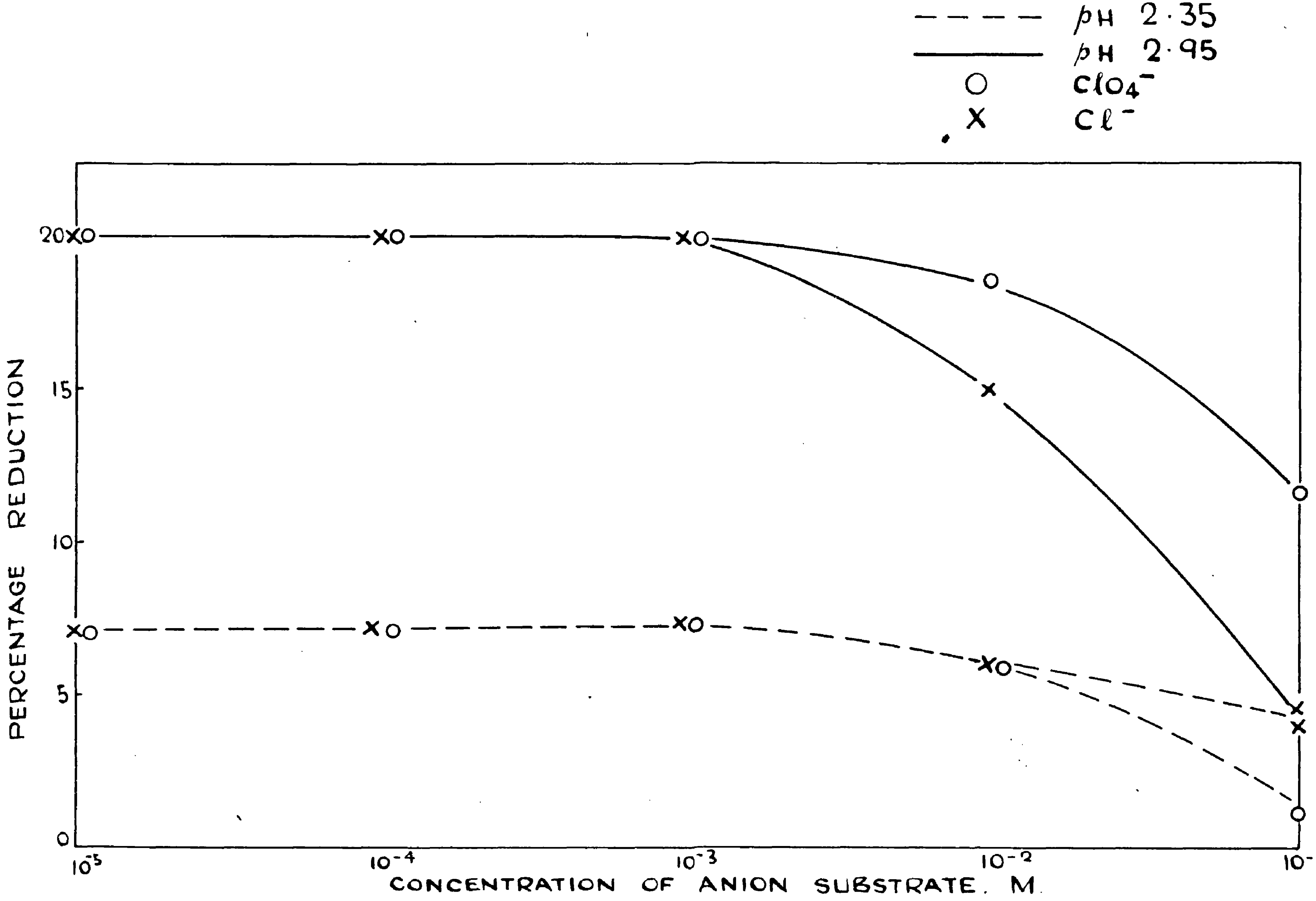
$\bar{M}$ of phosphate.			10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
Appearance of iron solution. ($1.3 \times 10^{-3} \bar{M}$)	(a)	before exposure	faint green clear	bright green clear	blue-green colloidal	blue-green colloidal	blue-green ppt.
	(b)	after exposure	faint green clear	bright green clear	blue-green colloidal	blue-green colloidal	-

Complex formation of iron with these anions is thus shown to decrease the photo-activity of the solutions very considerably.

The effect of added Cl^- is compared with ClO_4^- in Fig. 15. The first point to notice with the Cl^- is that its quelling of photo-activity only becomes significant as added $[Cl^-]$ approaches $10^{-2}\bar{M}$.

The next important feature is that while added ClO_4^- at high concentrations decreases the photo-activity the reduction still remains p_H dependent whereas with Cl^- the reduction becomes independent of p_H at high concentrations of Cl^-. This is evidence that the ion-pair $Fe^{3+}Cl^-$ is photo-active under these conditions as against

FIG 15. EFFECT OF Cl', ClO_4' ON PERCENTAGE REDUCTION.



a hydroxyl complex at lower Cl^- concentrations. The iron solutions at high $[Cl^-]$ are distinctly green.

Assuming the decrease in photo-activity is due to complex formation of the iron, then the complexing potency of these anions is in the order $PO_4^{3-} > SO_4^{2-} > Cl^- > ClO_4^-$.

Discussion.

A. The Photo-active Species in the Present System.

In the section of the work just described polychromatic light was used and since more than one iron species absorbs in the U.V., e.g. $Fe^{+3}(H_2O)_6$, $Fe^{3+}OH^-$, $Fe^{+3}Cl^-$.... the interpretation of the results may become very complex.

However, according to spectrophotometric results of previous workers[1],[2], the hydrated ferric ion $Fe^{+3}(H_2O)_6$ will be inactive with wavelengths $>$ 300 mμ. On the other hand if sufficient energy is supplied for the primary process

$$Fe^{+3}.H_2O \xrightarrow{h\nu} Fe^{+2}.H_2O^+$$

the hydrated ferric ion may be photo-active[3]. This was recently suggested by Dain and Kachan[4] who worked with high light intensities, high ferric ion concentrations and high acidities as described in Table 1 (page 57).

---

[1] Rabinowitch and Stockmeyer, J.A.C.S., 1942, 64, 335.

[2] Glickman, Dain and Kutsays, Zhur.Fiz.Chem., 1948, 22, 906.

[3] Uri, Chem.Rev., 1952, 50, 375.

[4] Dain and Kachan, Doklady.Akad.Nauk.,S.S.S.R.,1948,61, 471.

In the present work the photo-reduction greatly increases as the p_H is raised from 2.0 to 3.0. It would be expected to decrease if $Fe^{+3}(H_2O)_6$ is the photo-active species since hydrolysis would diminish the amount of this present. Moreover, using Pyrex flasks instead of quartz (1 mm. glass cuts off light less than about 310 mμ) photo-reductions of about the same magnitude as in quartz flasks were obtained. (Described later on page 109, Part 2.).

It is therefore most likely that an ion-pair is the photo-active species, absorbing about 300 mμ and above.

Evans and Uri[5] have postulated that the ion-pairs $Fe^{+3}Cl^-$ and $Fe^{+3}OH^-$ are photosensitive, their maximum absorption is in the region 300 mμ.

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

Since Cl^- is the anion used here, then ion-pair complexes of ferric ion with chloride will be present in solution, e.g. $Fe^{+3}Cl^-$, $FeCl_2^+$, $FeCl_3$.... From the results of Gamlen and Jordan[6] on ferric-chloro complexes

---

[5] Evans and Uri, Nature, 1949, 164, 404.

[6] Gamlen and Jordan, J.Chem.Soc., 1953, 1435.

it was adduced that in the present system, $[Cl^-] = 4x10^{-3}M$, the first association complex $Fe^{+3}Cl^-$ is the only one which should be considered.

Because of the relatively high p_H's studied primary hydrolysis should be quite extensive. The most complete investigation on the products of hydrolysis of the ion Fe^{+3} is that of Hedström[7] using new e.m.f. measurements developed by Biedermann and Sillen[8] and other workers for studying complex equilibria. They derived the following equilibrium constants for the 3 stages of hydrolysis:-

$$Fe^{+3} + H_2O \rightleftharpoons FeOH^{+2} + H^+ \qquad k_{11} = 9 \times 10^{-4}$$
$$Fe^{+3} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+ \qquad k_{12} = 5 \times 10^{-7}$$
$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{+4} + 2H^+ \qquad k_{22} = 1.22 \times 10^{-3}$$

It is seen that the formation of dimer. $Fe_2(OH)_2^{+4}$ is postulated.

Malay and Selwood[9] recently found further evidence of dimer formation in a magnetic and spectrophotometric study of ferric perchlorate solutions. It was found

---

[7] Hedström, Arkiv.Chemi., 1953, 6, 1.

[8] Biedermann and Sillen, Arkiv.Chemi., 1953, 5, 424.

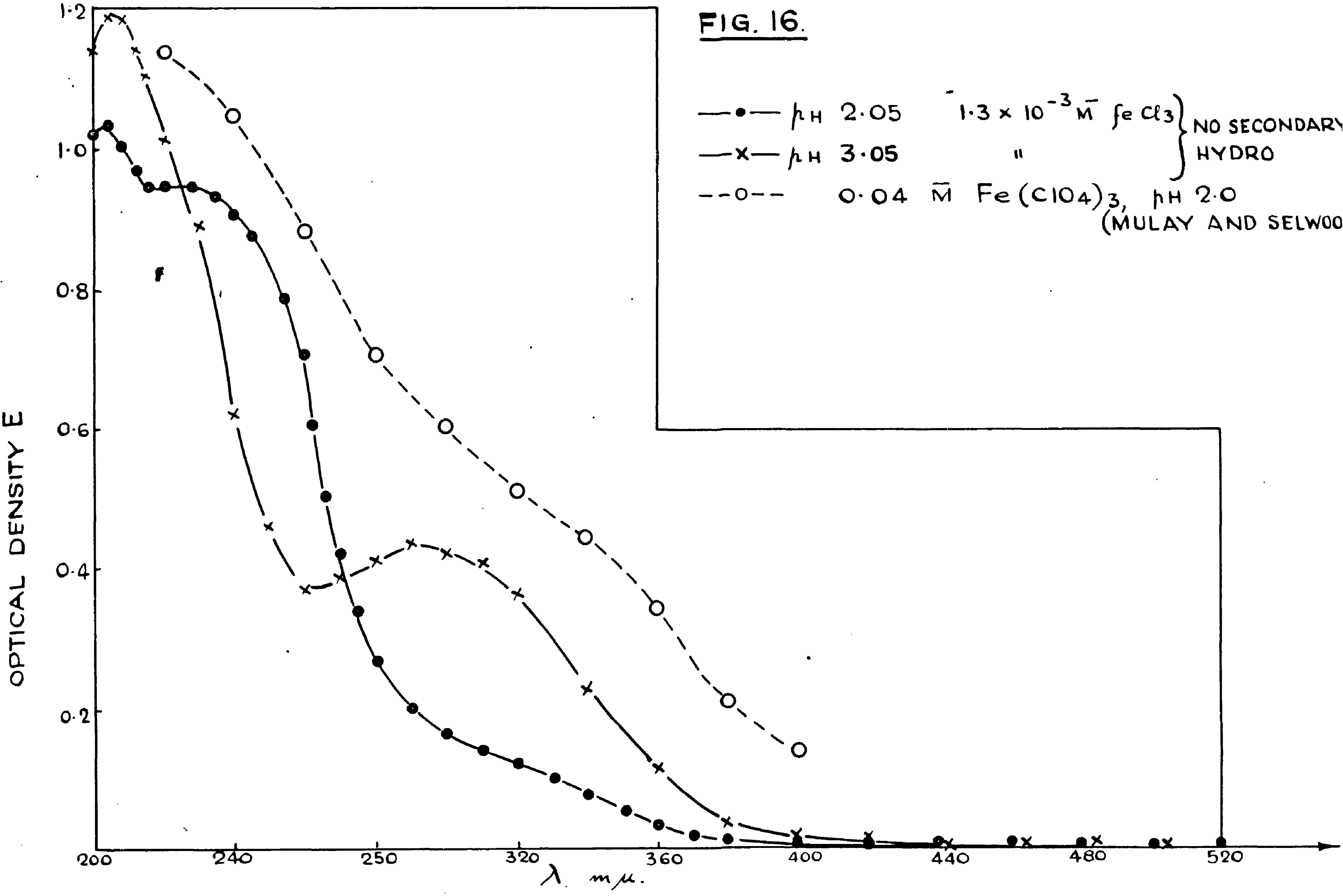
[9] Malay and Selwood, J.A.C.S., 1955, 77, 2693.

that the species $Fe_2(OH)_2{}^{4+}$, henceforth called the "dimer", is diamagnetic. In a quantitative interpretation of the absorption spectra it was shown that at high acidities the absorption band at 240 mμ is due solely to Fe^{+3}, that at lower acidities the ionic species $Fe^{+3}OH^-$ contributes to the absorbance at 240 mμ, and that the bond at 335 mμ is due solely to $Fe_2(OH)_2{}^{+4}$. This is in agreement with the observations of Glickman and co-workers[2].

Fig. 16 shows spectral curves for the present system $1.3 \times 10^{-3}\bar{M}$ ferric chloride in 2 mm. cells at p_H's 2.05 and 3.05 compared with one of 0.04 $\bar{M}$ ferric perchlorate at p_H 2.0 measured by Malay and Selwood. These authors state that with solutions of p_H greater than 1.8 only a broad absorption bond extending into the visible was found, without any definite peaks.

In the present investigation the spectral curves may be qualitatively described by accepting the conclusions of Glickman et al, and Malay and Selwood. At p_H 2.05, (attained by diluting the iron salt into $HClO_4$, not HCl), the high absorption in the U.V. between 200--260 mμ may be attributed to Fe^{+3} and $Fe^{+3}OH^-$. There

FIG. 16.


—●— pH 2·05 1·3 × 10⁻³ M̄ FeCl₃
—×— pH 3·05 "
NO SECONDARY
HYDRO
--○-- 0·04 M̄ Fe(ClO₄)₃, pH 2·0
(MULAY AND SELWOO
OPTICAL DENSITY E
1·2
1·0
0·8
0·6
0·4
0·2
200
240
250
320
360
400
440
480
520
λ mμ.

appear to be two peaks, one at 205 mu and one at 235 mu. It has been established by previous workers that the peak at 240 $m\mu$ is to be attributed to Fe^{+3} and further it is postulated that $Fe^{+3}OH^-$ contributes to this band. When the p_H is increased to 3.05 in the present system the intensity at 240 $m\mu$ decreases as would be expected
i/ ~~o~~f $Fe^{+3} \longrightarrow$ hydrolysis products, but the peak at 205 $m\mu$ increases as seen in Fig. 16. It is therefore suggested that this peak is due to $Fe^{+3}OH^-$.

Increase of p_H also leads to the formation of a strong band in the region 300 $m\mu$. This is somewhat lower than that of 335 $m\mu$ ascribed to $Fe_2(OH)_2{}^{4+}$. However, at this high p_H of 3.05, where hydrolysis of the iron to ferric hydroxide is imminent, hydrolytic species of a higher order may be present, e.g. $Fe(OH)_2{}^+$, and contribute to the absorbance in this region, and moreover polynuclear formation may play an important part.

With these restrictions in mind, let it be assumed that the absorbance in the region 300 $m\mu$ is due mainly to $Fe_2(OH)_2{}^{4+}$.

Therefore, in the absence of secondary hydrolysis, the species $Fe^{+3}Cl^-$ and $Fe_2(OH)_2{}^{4+}$ are the ones to which the photo-activity of the solution may be ascribed. The appearance of secondary hydrolysis of the solution leads to an increase in photo-activity. The role of colloidal ferric hydroxide is discussed later in Part 4, of this thesis.

It is necessary to show, if possible, to what extent each of the species $Fe^{+3}Cl^{-}$, $Fe_2(OH)_2{}^{4+}$ contribute to the photo-activity.

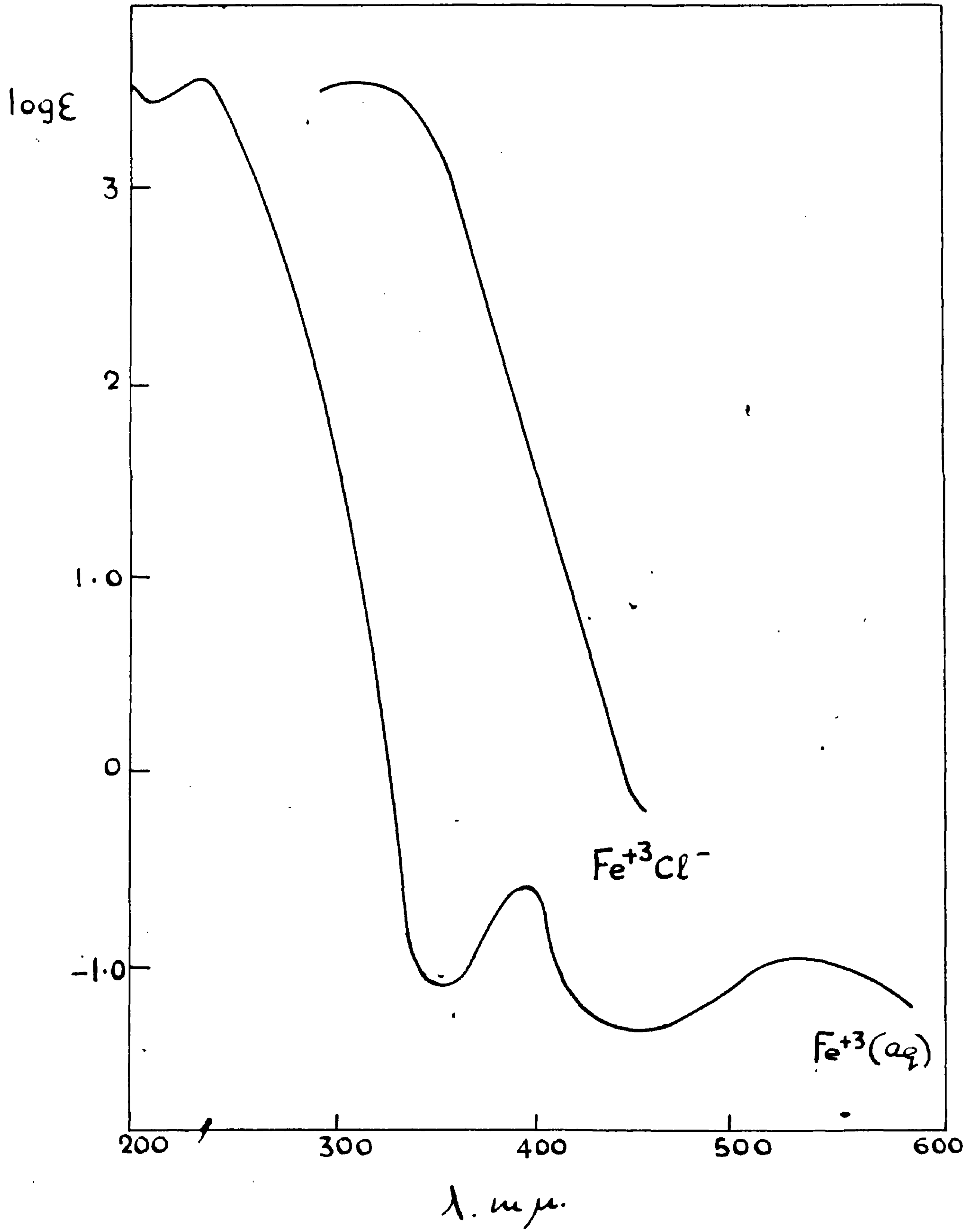
B. The Photochemically Active Species and the Absorption Fraction.

The absorption spectra of the hydrated ferric ion $Fe(H_2O)_6{}^{3+}$ and of the complex, $Fe^{3+}Cl^{-}$, determined by Rabinowitch and Stockmeyer are given in Fig. 17.

It is seen that the peak for $Fe^{+3}Cl^{-}$ is about 320-340 mμ and the absorption decreases quickly as the wavelength is increased. Malay and Selwood[9] have shown that the 'dimer" $Fe_2(OH)_2{}^{4+}$ has a maximum absorption at 335 mμ and it too shows a decrease in absorbance as the wavelength is increased.

Thus for both species photo-activity should be evident in the region 300-350 mμ and perhaps at even

FIG. 17



slightly higher wavelengths.

h/ The extent to which a species will s~~l~~ow photo-activity will of course depend on the amount of light it absorbs, and therefore a comparison of the absorption fractions of the two species, say at 335 mμ, will indicate their individual contribution to the photo-activity of the iron solution as a whole.

Assuming that at p_H's 2.05 and 3.05 the only species absorbing at this wavelength are Fe^{+3}, $Fe^{+3}Cl^-$ and $Fe_2(OH)_2{}^{4+}$, then from a knowledge of their concentrations and from known values of their molar extinction coefficients (ε) at 335 mμ, their respective light absorption fractions can be evaluated thus:-

Light absorption Fraction $$\alpha_1 = \frac{C_1\varepsilon_1}{C_1\varepsilon_1 + C_2\varepsilon_2 + C_3\varepsilon_3}$$

let $[Fe^{+3}]$	=	C_1	at 335 mμ	$\varepsilon_1 = 0.22$	Rabinowitch and Stockmeyer[1] (Fig. 1.)
$[Fe^{+3}Cl^-]$	=	C_2	and T = 25°C.	$\varepsilon_2 = 3160$	
["dimer"]	=	C_3		$\varepsilon_3 = 25000$	Malay and Selwood[9].

The actual values given by Malay and Selwood for ε_3 are 8.3×10^4 at 15°C. and 2.5×11^4 at 51°C. Rabinowitch and Stockmeyer made their measurements at 25°C. A value for α_3 of 2.5×10^4 was taken and consequently the calculated value of α_3 will be a minimum value.

(1). $\underline{p_H\ 3.05}$.

The solution used was $1.3 \times 10^{-3}\bar{M}$ ferric chloride.

let total iron = $[Fe^{+3}]_0 = 1.3 \times 10^{-3}\bar{M}$

$[H^+] = 8.9 \times 10^{-4}\bar{M}$

total chloride = $[Cl^-]_0 = 3.9 \times 10^{-3}\bar{M}$

The following equilibria must be considered

(a) $Fe^{+3} + H_2O \rightleftharpoons Fe^{+3}OH^- + H^+$ $\quad k_{11} = 9\times10^{-4}$ Hedstrom[7]

(b) $2Fe^{+3} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$ $\quad k_{22} = 1.22\times10^{-3}$

(c) $Fe^{+3} + Cl^- \rightleftharpoons Fe^{+3}Cl^-$ $\quad K = 30$ Rabinowitch, Stockmeyer[1].

$$\text{(a)} \quad k_{11} = \frac{[Fe^{+3}OH^-].[H^+]}{[Fe^{+3}]}$$

$$\therefore \quad [Fe^{+3}OH^-] = k_{11}.\frac{[Fe^{+3}]}{[H^+]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\text{(b)} \quad k_{22} = \frac{[\text{Dimer}].[H^+]^2}{[Fe^{+3}]^2}$$

$$\therefore \quad [\text{Dimer}] = k_{22}.\frac{[Fe^{+3}]^2}{[H^+]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

(c) $$K = \frac{[Fe^{3+}Cl^-]}{[Fe^{+3}][Cl^-]}$$

$$\therefore \quad [Fe^{+3}Cl^-] = K.[Fe^{+3}][Cl^-].$$

but $[Fe^{+3}Cl^-] + [Cl^-] = [Cl^-]_o$

i.e. $K.[Fe^{+3}][Cl^-] + [Cl^-] = [Cl^-]_o$

$$\therefore \quad [Cl^-][1 + K[Fe^{+3}]] = [Cl^-]_o$$

$$\therefore \quad [Cl^-] = \frac{[Cl^-]_o}{1 + K[Fe^{+3}]}$$

$$\therefore \quad [Fe^{+3}Cl^-] = \frac{K.[Fe^{+3}].[Cl^-]_o}{1 + K[Fe^{+3}]} \quad \ldots\ldots(3)$$

but $[Fe^{+3}] + [Fe^{+3}OH^-] + [Dimer] + [Fe^{+3}Cl^-] = [Fe^{+3}]_o$

$$\therefore \quad [Fe^{+3}] + k_{11}\frac{[Fe^{+3}]}{[H^+]} + k_{22}\frac{[Fe^{+3}]^2}{[H^+]^2} + \frac{K[Fe^{+3}][Cl^-]}{1 + K[Fe^{+3}]} = [Fe^{+3}]_o$$

Since $30[Fe^{+3}] \ngtr 30[Fe^{+3}]_o = 30 \times 1.3 \times 10^{-3} = 0.039$

Then $1 + 30\,[Fe^{+3}] = 1.$

$$\therefore \quad [Fe^{+3}] + k_{11}\frac{[Fe^{+3}]}{[H^+]} + k_{22}\frac{[Fe^{+3}]^2}{[H^+]^2} + K.[Fe^{+3}][Cl^-]_o = [Fe^{+3}]_o$$

$$\therefore \quad [Fe^{+3}] + \frac{9 \times 10^{-4}}{8.9 \times 10^{-4}}.[Fe^{+3}] + \frac{1.22 \times 10^{-3}}{[8.9 \times 10^{-4}]^2}[Fe^{+3}]^2 +$$

$$+ 30 \times 3.9 \times 10^{-3}[Fe^{+3}] = 1.3 \times 10^{-3}$$

$$\therefore\ 1.54 \times 10^{5}\ [Fe^{+3}]^{2} + 2.117\ [Fe^{+3}] - 1.3 \times 10^{-3} = 0.$$

solving this quadratic gives $[Fe^{+3}] = 4.61 \times 10^{-4}\bar{M}$.

and by substitution in (1), (2) and (3)

$$[Fe^{+3}OH^{-}] = 4.66 \times 10^{-4}\bar{M}$$

$$[\text{Dimer}] = 3.3 \times 10^{-4}\bar{M}$$

$$[Fe^{+3}Cl^{-}] = 0.54 \times 10^{-4}\bar{M}$$

considering the species Fe^{+3}, $Fe_2(OH)_2{}^{4+}$ and $Fe^{+3}Cl^{-}$ which are assumed to be the only ones absorbing at 335 mμ.

Then if $C_1 = [Fe^{+3}] = 4.61 \times 10^{-4}$ $\qquad \varepsilon_1 = 0.22$

$C_2 = [Fe^{+3}Cl^{-}] = 0.54 \times 10^{-4}$ $\qquad \varepsilon_2 = 3160$

$C_3 = [\text{Dimer}] = 3.3 \times 10^{-4}$ $\qquad \varepsilon_3 = 25000$

$$\text{Then } \alpha_1 = \frac{C_{1\ \ 1}}{C_1\varepsilon_1 + C_2\varepsilon_2 + C_3\varepsilon_3} = \frac{9.2 \times 10^{-5}}{8.42} = 0.0$$

$$\alpha_2 = \frac{C_{2\ \ 2}}{C_1\varepsilon_1 + C_2\varepsilon_2 + C_3\varepsilon_3} = \frac{0.17}{8.42} = 0.02$$

$$\alpha_3 = \frac{C_{3\ \ 3}}{C_1\varepsilon_1 + C_2\varepsilon_2 + C_3\varepsilon_3} = \frac{8.25}{8.42} = 0.98.$$

(2) $\underline{p_H\ 2.05.}$

This lower p_H was achieved using $HClO_4$.

$\therefore$ as before $[Fe^{+3}]_b = 1.3 \times 10^{-3}\bar{M}$

but $[H^{+}] = 8.9 \times 10^{-3}\bar{M}$

The calculation is then identical with that above, and it is found

$$\alpha_1 = 0.0$$
$$\alpha_2 = 0.565$$
$$\alpha_3 = 0.435$$

(3) p_H 2.5.

$$[H^+] = 3.16 \times 10^{-3}$$
$$\alpha_1 = 0.0$$
$$\alpha_2 = 0.14$$
$$\alpha_3 = 0.86$$

The concentrations of the species Fe^{+3}, $Fe^{+3}OH^-$, $Fe_2(OH)_2{}^{4+}$ and $Fe^{+3}Cl^-$ at p_H's 2.05, 2.5 and 3.05 are summarised in Table 5 , together with absorption fractions of light of λ 335 mμ.

TABLE 5.

Summary of concentrations and absorption fractions of the ions in the solution 1.3×10^{-3} $FeCl_3$ at various p_H values.

p_H	Concentration in Moles Litre x 10^4				Absorption Fraction α, at 335 mμ		
	Fe^{+3}	$Fe^{+3}OH^-$	$Fe_2(OH)_2{}^{+4}$	$Fe^{+3}Cl^-$	Fe^{+3}	$Fe_2(OH)_2^{+4}$	$Fe^{+3}Cl^-$
2.05	10.6	1.06	0.14	1.52	0.0	0.435	0.565
2.50	8.75	2.5	0.94	1.02	0.0	0.86	0.14
3.05	4.61	4.66	3.3	0.54	0.0	0.98	0.02

The photo-reduction increases with increase of p_H. According to the above calculations only two species increase in concentration with decreasing acidity - $Fe^{+3}OH^-$ and $Fe_2(OH)_2^{+4}$. The absorption fraction of the dimer at 335 mμ $\gg$ than that of $Fe^{+3}Cl^-$ at p_H 2.5 and above, and the increase in absorbance can be directly correlated with the increase in photo-activity of the solution. It may well be that the ion-pair $Fe^{+3}OH^-$ absorbing at about 200-240 mμ contributes to the photo-reduction but this cannot be ascertained with the present apparatus. However, it is beyond doubt that the species $Fe_2(OH)_2^{+4}$ is photo-reduced.

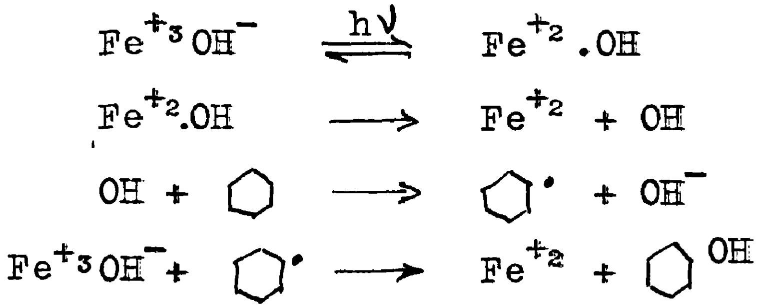
C. The Oxidation of Organic Substrates.

The addition of benzene and benzoic acid as substrates led to the hydroxylation of the benzene nucleus.

This is strong experimental evidence that it is a hydroxyl complex which is the photo-active species (an OH radical being produced by photo-dissociation). Formation of OH radicals from a thermal reaction of a Cl atom,

i.e. $Cl + OH^- \longrightarrow Cl^- + OH$, produced by a photo-dissociation of $Fe^{+3}Cl^{-}$, although thermodynamically feasible, is unlikely because of the low concentration of OH^{-} ion. ($\sim 10^{-11}$ g.-ions litre).

This photo-oxidation of benzene and benzoic acid has been carefully studied, the former by Baxendale and Magee[10] and the latter substrate by Bates, Evans and Uri[11]. The monochromatic light used by these workers was of 313 mμ and 365 mμ. It was considered at that time that the ion-pair $Fe^{+3}OH^{-}$ absorbs in this region. Their mechanism is as follows



However, the recent work of Malay and Selwood[9] provides very strong evidence that it is the "dimer" that absorbs in this region and the initial step should be modified to

$$Fe_2(OH)_2^{+4} \xrightarrow{h\nu} Fe^{+3}OH^{-} + Fe^{+2} + OH$$

Moreover, a rather important possibility becomes evident, that of an intramolecular breakdown of the

---

[10] Baxendale and Magee, Trans.Farad.Soc., 1955, 51, 205.

[11] Bates, Evans and Uri, Nature, 1950, 166, 869.

dimers, on light absorption, as follows

$$Fe_2(OH)_2{}^{4+} \xrightarrow{h\nu} 2Fe^{+2} + H_2O_2$$

The hydrogen peroxide formed would of course complicate a kinetic analysis of the system due to the large number of possible reactions,

$$\text{e.g.} \quad Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH$$

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

etc.

but a postulation of this intramolecular reaction might account for the lack of oxidation balance found by Baxendale and Magee, discussed earlier on page 68

This formation of hydrogen peroxide would be independent of substrate concentration since it is an intramolecular decomposition. The H_2O_2 would not attack the organic substrate directly and its decomposition to oxygen would be catalysed by the iron solution, i.e. the lack of oxidation balance may be due to the photo-oxidation of water.

D. Photo-Reduction in the Absence of Added Substrate.

In the present system, a photo-reduction is found without the addition of substrate.

The effect of p_H and the addition of Fe^{+2} indicate that the results can be explained with the generally accepted reaction scheme

$$\begin{bmatrix}\text{Ferric Hydroxyl}\\ \text{Complex}\end{bmatrix} \underset{\text{THERMAL}}{\overset{h\nu}{\rightleftarrows}} Fe^{+2} + OH \ldots\ldots\ldots\ldots(a)$$

$$OH + SUBSTRATE \longrightarrow PRODUCTS \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

and calculation of relative absorption fractions has shown this complex to be $Fe_2(OH)_2{}^{4+}$, although $Fe^{+3}OH^-$ may contribute to the photo-reduction as well.

When the $[Fe^{+2}]$ reaches a certain level an equilibrium ~~sets in~~ is reached as described by equation (a).

Since there is a net reduction of the ferric iron an oxidisable substrate must be present in solution.

Previous workers attributed this reduction to oxidation of organic impurities in the distilled water. (N.B. There is no evidence in the literature of previous work at p_H's > 2.0).

In the present work this is not considered to be the case, for a number of reasons.

(1) Reduction values were reprodubicle in experiments over many months in systems prepared from several batches of A.R. $FeCl_3.6H_2O$ and water purified by a variety of methods.

(2) Back oxidation to Fe^{+3} of photo-produced Fe^{+2} by the addition of a small excess of concentrated H_2O_2 and reirradiation, after a period of standing to allow decomposition of excess H_2O_2, gave the same stationary percentage reduction as before. Three repetitions of this alternate exposure and oxidation of this same solution produced in no instance any significant difference in the yield of Fe^{+2}. Whatever small amount of organic impurities may be supposed to have been present, it should have been, by the successive exposures, very greatly decreased with consequent marked influence on the yield of Fe^{+2}.

(3) The effect of added glucose and benzoic acid in the photo-reduction is shown in Figs. 12, 13. It is seen that the variations which are given for these substrates are linear and <u>parallel,</u> which means that a given quantity of given (added) substrate produces the same increment of reduction whatever the p_H of the system may be in the range studied. It is therefore difficult to see why the reduction in the absence of added substrate should be strongly p_H dependent ~~or~~ if it is a consequence of oxidisable organic impurities already there.

It was therefore decided that this photo-reduction was an inherent property of the iron solution, the substrate being one of the ions or ion-pairs.

After the initial formation of OH free radicals plausible reactions are

(a) $OH + Cl^- \longrightarrow OH^- + Cl$

and $2Cl \longrightarrow Cl_2$

or $Fe^{+3}Cl^- + Cl \longrightarrow Fe^{+2} + Cl_2$

The radiolysis of aqueous solutions of halide ions has been discussed by Allen[12]. Reactions of the type

$$OH + X^- \longrightarrow OH^- + X$$

are postulated.

(b) $OH + OH \longrightarrow H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

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

$\longrightarrow H_2O + \frac{1}{2}O_2$

Uri[13] suggests that in the photo-oxidation of water by ferric iron the two competing reactions would be

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

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

---

[12] Allen, J.Phys.and Colloid.Chem., 1948, 52, 479.

[13] Uri, Chem.Rev., 1952, 50, 375.

Whatever the mechanism, it seemed likely that there was either an oxidation of chloride to chlorine or an oxidation of water to oxygen or perhaps both.

The investigation was therefore pursued with the intention of trying to detect these possible reaction products.

PART 2.

THE DETECTION AND IDENTIFICATION OF PHOTOCHEMICALLY-PRODUCED OXYGEN.

Introduction.

Having concluded that the photo-reduction of ferric to ferrous ion in aqueous solutions of ferric chloride in the absence of added substrate was not due to the nominal presence of oxidisable organic impurities (described in PART 1) it was deduced that the most likely products were chlorine and/or oxygen.

This section of the thesis describes how no chlorine was found but that a photo-produced gas, non-condensible in liquid oxygen, was detected and shown to be oxygen, affirming that photo-oxidation of water by ferric iron is taking place.

The detection of chlorine was attempted using a starch-iodide method. Ferric iron itself oxidises iodide to iodine under certain conditions and it was therefore found necessary to remove any dissolved chlorine from the iron solution before analysis. This was done by carefully distilling the irradiated iron solution into a receiver containing KI starch solution.

Kautsky and Hirsch[1] showed that the phosphorescence excited in certain dyes adsorbed on silica-gel, e.g. try-

---

[1] Kautsky and Hirsch, <u>Zeits.f.anorg.allgem.Chemie</u>, 1935, <u>222</u>, 126.

paflavine, Uranin, is strongly quenched by small partial pressures of oxygen. With trypaflavine, at 5 x 10^{-4} mm. of oxygen the intensity of the green phosphorescence was considerably reduced, and the phosphorescence was entirely suppressed by oxygen at 3 x 10^{-3} mm. Kautsky also studied the quenching action of other gases and found that the phosphorescence is strongly quenched by both water and ammonia.

Meyer and Rouge[2] measured the time during which the after-glow could be visibly perceived after the exciting radiation was cut off. They detected a shortening of the period at a partial pressure of only 3 x 10^{-4} mm. of oxygen. The quenching process is connected with a photochemical reaction by which oxygen is consumed and the dyestuff oxidised.

The application of Kautsky's method, using a trypaflavine phosphor has been discussed in detail from the experimental and theoretical view points by Franck and Pringsheim[3]. They commented that the quenching of phosphorescence by water and ammonia is surprising, since

---

[1] Kautsky and Hirsch, Zeits.f.anorg.allgem.Chemie., 1935, 222, 126.

[2] Meyer and Rouge, Zeits.f.angew.Chemie.,1939,52, 637.

[3] Franck and Pringsheim. J.Chem.Phys., 1943, 11, 21.

it is difficult to imagine that the excited dye molecule can react with water and ammonia if only 60 k.cal. are available as excitation energy. It was in fact shown that water vapour does not quench the phosphorescence. They suggest that the quenching described by Kautsky is due to oxygen liberated from the gel by a process in which strongly adsorbed oxygen molecules are dislodged by water molecules. Ammonia is adsorbed by the gel during its preparation by Kautsky's method. Franck and Pringsheim found that this ammonia is more difficult than oxygen to remove from the gel, and they concluded that the quenching action of ammonia observed by Kautsky, like the apparent quenching by water vapour, was probably due to oxygen. As to the mechanism of phosphorescence it was suggested, as a hypothesis, that hindrance of the natural movement of the atoms in the dye molecule causes a delay in the internal conversion of excitation energy into molecular oscillation energy, thus favouring the re-emission of light. The green phosphorescence of Trypaflavine adsorbed on silica-gel was half-quenched by oxygen at 5×10^{-5} mm. pressure, the quenching at higher oxygen pressures was much smaller than expected.

It was suggested this indicated that two long-lived excitation states (tautomers of trypaflavine) share in causing the green phosphorescence. The first (M_1) is very sensitive to oxygen, whereas the second (M_2) is insensitive. The phosphorescence still visible at the higher oxygen pressures owes its origin entirely to M_2.

In a later study, on the photo-synthetic production of oxygen in algae illuminated by flashes of light, Pollack, Pringsheim and Terwood[4] successfully employed the phosphor method to measure oxygen evolution as low as 5×10^{-8} c.c. at atmospheric pressure per minute.

More recently the technique was used by Zimmerman[5] for a kinetic study of the photo-production of oxygen from solutions of potassium permanganate.

Dain and Kachan[6] have measured gas evolution (oxygen) from ferric perchlorate solutions of high acidity, (0.3 M Fe^{+++}, 0.1–5.0 M $HClO_4$), irradiated with light of $\lambda > 3650$. They attribute this photo-oxidation to $[Fe(H_2O)_6]^{3+}$. Their higher rate was 5×10^{-2} $mm.^3$ min. A vacuum method was used which enabled the

---

[4] Pollock, Pringsheim and Terwood, J.Chem.Phys., 1944, 12, 295.

[5] Zimmerman, J.Chem.Phys., 1955.

[6] Dain and Kachan, Doklady Akad.Nauk.S.S.S.R., 1948, 61, 471.
Chem.Abs., 1948, 42, 8659.

measurement of small amounts of gas by change of pressure above the previously exposed and frozen solution. Repeated freezing, evaluation, thawing, resulted in degassing of the solution. After exposure the solution was frozen and thawed several times and the evolved gas pressures were measured on a McLeod gauge.

In the present work a photo-produced non-condensible gas was detected using Dain and Kachan's technique. The quenching of phosphorescence of Uranin adsorbed on silica-gel was used to identify the gas as oxygen. By way of confirmation the gas was sparked with hydrogen; subsequent combination in the volume ratio 2 of H_2 1 of gas verified that the gas was oxygen.

Experimental and Results.

(A). The Search for Chlorine.

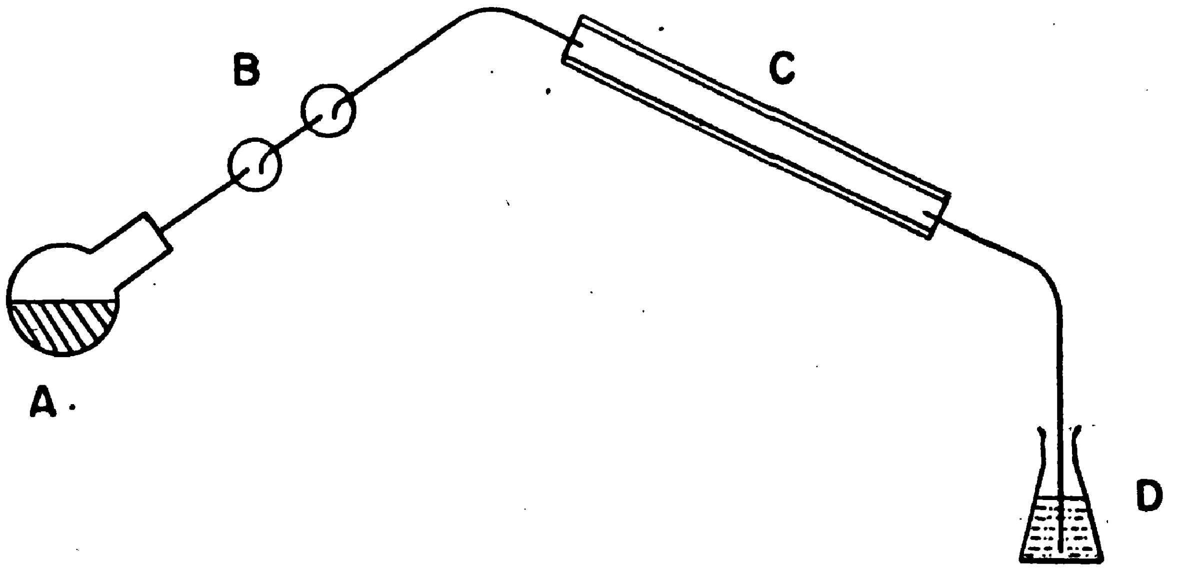
At p_H 3.05 a $1.3 \times 10^{-3}\bar{M}$ ferric chloride solution undergoes 30% reduction with a 10 hour exposure, i.e. ferrous ion produced = $3.9 \times 10^{-4}\bar{M}$. Assuming that chlorine was the only oxidation product, then chlorine in solution = $1.95 \times 10^{-4}\bar{M} = 2 \times 10^{-4}\bar{M}$ (1 mole $Cl_2 \equiv 2$ moles Fe^{++}).

For the estimation of such small quantities a starch-iodide method was decided upon. The iron solution could not be tested directly with starch iodide reagent since the reaction $Fe^{+++} + \bar{I} \rightarrow Fe^{++} + \frac{1}{2}I_2$ takes place. The addition of F^- (as potassium fluoride) did inhibit this reaction at this p_H used, presumably due to complexing of the ferric iron, and standard iron chlorine solutions were shown to give a blue colour. However for high reduction of the iron, high p_H's had to be used with consequent hydrolysis of the solution on irradiation. It was thought necessary to dissolve the ferric hydroxide to allow a quick complexing with F^- to take place and also to rule out the possibility of chlorine being occluded by the colloid. Concentrated sulphuric acid was added to make the solution 2 $\bar{M}$ in acid. At this high acidity the F^- no longer inhibited the Fe^{+++}/I^- reaction.

An obvious alternative was to free any dissolved chlorine in solution by boiling. The sensitivity of this method was determined by standard iron/chlorine solutions. The apparatus (Fig.18) consisted of a quartz flask 'A' (the irradiation vessel), containing the iron chlorine solutions. All the standard iron chlorine solutions used had been hydrolysed to simulate the final condition of an irradiated solution. Before distillation 4 ml. of conc. H_2SO_4 was added to 150 ml. of the iron chlorine solution to dissolve the ferric hydroxide (which may have occluded some chlorine). This acid solution was then distilled into 25 ml. of a starch -iodide solution (D) until about 10 ml. of water came over, the splash head (B) being interposed. 'C' is a spiral condenser. All joints were of Quickfit and no evolved gas could escape before passing through the starch iodide solution.

A stock solution of chlorine water was prepared by bubbling cylinder chlorine through distilled water. This solution was standardised by sodium thiosulphate

FIG. 18. CHLORINE DETECTION APPARATUS



which had been previously standardised with potassium iodate[7]. The chlorine solution was found to be 2.8 x $10^{-2}\bar{M}$. Dilution of this into the iron solution gave the standard iron chlorine solutions. The iron concentration was kept constant at 1.3 x $10^{-3}\bar{M}$ and $p_H = 3.05$.

A starch solution was prepared by stirring a paste of 1 g. of starch with 100 ml. of boiling water. The starch iodide reagent was 1 ml. starch + 24 ml. 10% K.I. solution. Fresh starch solutions were prepared daily.

Table 1 indicates the sensitivity of the colorimetric test with a volume of 150 ml. of solution being used for distillation.

TABLE 6.

$\bar{M}$ of Cl_2 in Fe^{+++} solution.	Colour of Starch KI soln.
3 x 10^{-6}	colourless
6 x 10^{-6}	colourless
1.5 x 10^{-5}	faint blue
4.5 x 10^{-5}	blue
10^{-4}	blue

---

[7] Vogel, 'Quantitative Inorganic Analysis.'

It is seen that chlorine in the iron solution can be detected with certainty at concentrations $\geqslant 1.5 \times 10^{-5}\bar{M}$. The calculated maximum molarity of chlorine to be expected from irradiated ferric chloride solutions is $\sim 2 \times 10^{-4}\bar{M}$ as previously calculated, i.e. easily detectable by this method, and even concentrations as small as $\frac{1}{10}$ th. of this value can be shown to be present.

The detection of chlorine in irradiated iron solutions was then attempted. The colorimetric test proved negative, i.e. if at all present the $[Cl_2] < 1.5 \times 10^{-5}\bar{M}$. The iron was 30% reduced.

The effect of initially added chlorine on the photo-reduction was investigated. Chlorine of $\bar{M} = 2 \times 10^{-4}\bar{M}$ was irradiated for 5 hrs. with $1.3 \times 10^{-3}\bar{M}$ ferric iron at p_H 3.05. Before irradiation a sample was tested by the starch-iodide distillation.technique and a blue colour obtained. Indeed the chlorine in the cold iron solution could easily be detected by smell. After irradiation no smell of chlorine was left. The starch-iodide distillation analysis proved negative, i.e. the amount of chlorine had fallen from $2 \times 10^{-4}\bar{M}$ to $\leqslant 1.5 \times 10^{-5}\bar{M}$. A small decrease was found in the photo-

-reduction of the iron; 24.4% without chlorine falling to 22.0% with chlorine initially present.

Thus it may be concluded that chlorine is not the main oxidation product, if formed at all, for, indeed, initially added chlorine is found to disappear on irradiation.

(B). The Detection of a Photo-Produced Gas.

In the photo-reduction of a 1.3×10^{-3}M ferric chloride solution at p_H 3.05 a maximum yield of 4×10^{-4} moles litre of ferrous ion is found ($\equiv$ 30% reduction), i.e. 6×10^{-5} moles in 150 ml. of solution.

The stoichiometry of the equation

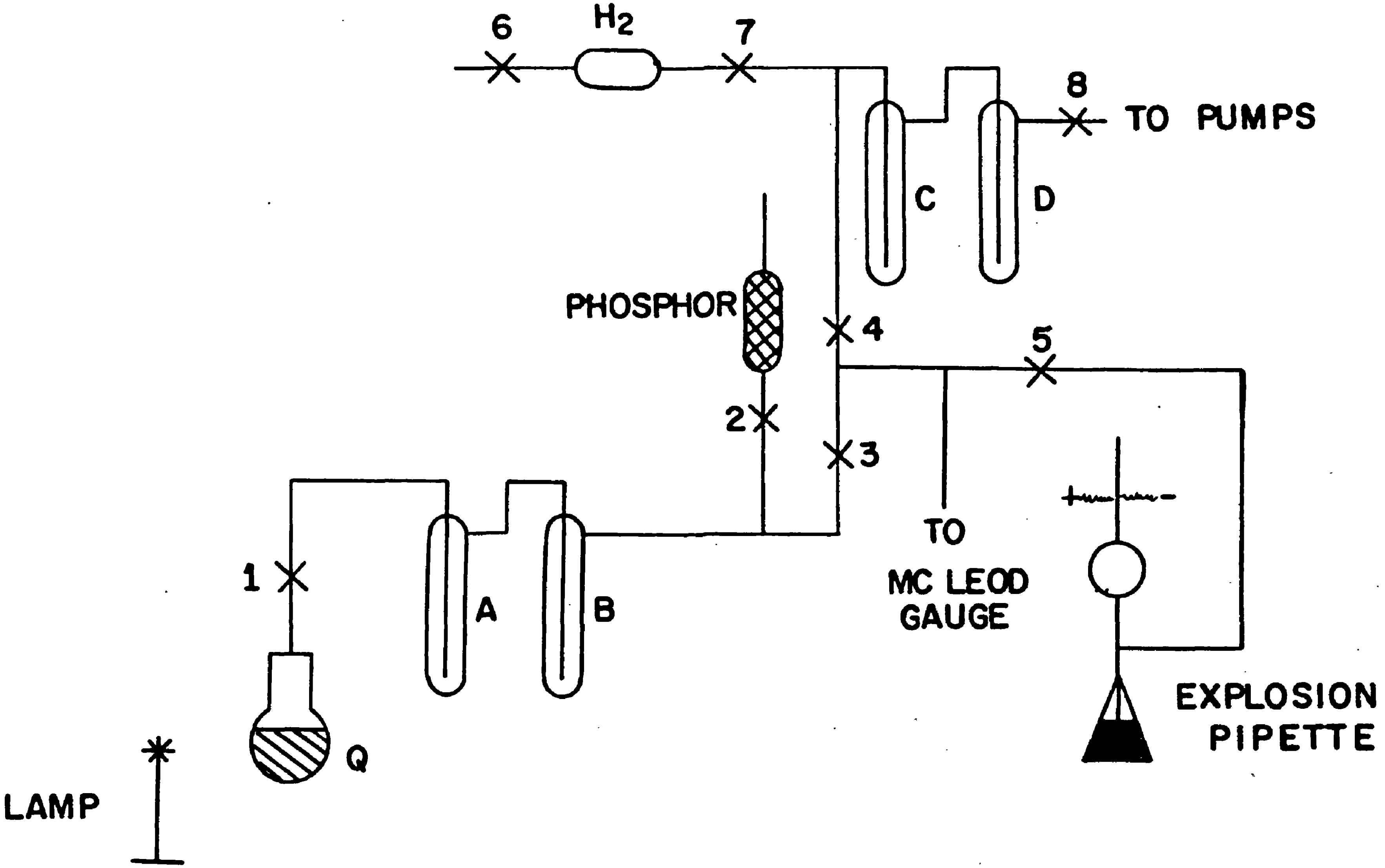
$$[2Fe^{+++} + H_2O = 2Fe^{++} + 2H^+ + \tfrac{1}{2}O_2]$$

shows that for every mole of oxygen formed, 4 moles of ferrous ion are produced, i.e. in 150 ml. of irradiated solution a maximum of 1.5×10^{-5} moles of oxygen may be expected.

Although the amount of gas expected with the present system was much greater than that of Dain and Kachan, it was decided to adopt their technique for the detection of any photo-produced gas. The high vacuum system constructed would also serve for the identification of any gas found, as oxygen for example, by the phosphor method of Kautsky.

The apparatus used for measuring the evolution of gas and identifying it is shown in Fig. 19. All taps were greased with Apiezon 'N' high vacuum grease, but the socket cone joints were fixed using picien, even z/ the B.34 cone socket joint of the quart~~y~~ flask (Q) onto the vacuum system. This was found necessary because the Apiezon grease tended to harden and become streaky when above a liquid-oxygen trap with consequent failure of the vacuum. This effect was greatly accentuated with the joint on the quartz flask since the freezing of the 150 ml. of iron solution it contained caused the evaporation of a considerable quantity of liquid oxygen. It was of course realised that contamination of the iron solution by picien vapour (from the hot picien) might occur, but care was taken when making the B.34 cone socket joint. The procedure adopted was to heat the cone on the vacuum system, and picien smear~~ed~~ round it; the <u>clean</u> socket of the flask was then heated and the joint made with slow rotation such that the picien did not reach the bottom of the joint. The flask was held in position until the joint was cool and thereafter

FIG. 19 HIGH VACUUM APPARATUS FOR GAS ANALYSIS



clamped. It was considered that contamination by picien would be at a minimum. However 'the end justified the means' as the results below indicate.

z/ A volume of 150 ml. of iron solution in the quartz irradiation flask (capacity 300 ml.) was saturated with oxygen-free nitrogen before irradiation. This gas (supplied by the British Oxygen Co.) had the specification $O_2 < 10$ p.p.m.. It was bubbled from the cylinder through a scrubber of acid permanganate then through two wash bottles containing distilled water. With nitrogen still bubbling through the solution the air-space between Tap 1 (closed) and the end of the B.34 cone (its picien smeared on ready) was flushed out with nitrogen. The B.34 socket had in the meantime been heated and the joint was quickly made onto the vacuum system. The amount of oxygen then remaining in solution was considered to be negligible. The nitrogen atmosphere above the solution was pumped off 5 minutes later.

The removal of oxygen before degassing the solution was not absolutely necessary as was later found but this refinement was continued.

The solution was degassed as follows:-

With taps 1,3,4 and 8 open (all others closed) the solution was boiled under vacuum till the pressure on the McLeod gauge read approx. 10^{-4} mm. (i.e. non-condensible gas). This took one minute. About 4 ml. of water distilled over into liquid-oxygen trap A during this operation.

Tap 1 was then closed and the solution frozen with liquid oxygen. The experimental technique of degassing the solution by freezing, evacuation, thawing cycles proved rather difficult at this point due to the large volume of solution (150 ml.) that was used, in comparison with the volume of 3 ml. used by Dain and Kachan. It was considered that this large volume was necessary in order that a reasonable quantity of photo-produced gas would be available for measurement and identification. In the early work the freezing of the solution was attempted with ethanol 'drikold'. This, however, proved disastrous for the quartz flasks, because the cooling of the solution was slow enough to allow the freezing to take place from the top down, and internal stresses in the ice water mixture, due to expansion of the water on freezing, cracked the bottom of more than one quartz flask. With liquid oxygen the rate of cooling of the solution was so fast that freezing took place from the bottom of the flask upwards.

While the iron solution was frozen trap A was temporarily dismantled and the water removed.

The apparatus was again put under high vacuum (10^{-5} mm.), tap 4 closed, i.e. pumps cut off, tap 1 opened and the pressure of gas released by the freezing of the solution, was measured on the McLeod. Tap 4 was then opened and the gas above the frozen solution pumped off to 10^{-5} mm. and tap 1 closed.

The frozen iron solution was now allowed to heat up very slowly in air for 10 minutes, before a water bath at 20°C. was put under it to hasten the melting. Any attempt to shorten this period of warming in the air

z/ visually resulted in cracking of the quartz flask. The total time to complete the melting was about 30 minutes.

This procedure of freezing, measurement of pressure above the solid, evacuation and thawing was repeated until the partial pressure above the solid was small. (About 4 freezings).

The solid was then liquefied and the iron solution irradiated for 30 minutes with the Hanovia S.500 lamp at a distance of 8 cm. At the high p_H this exposure time was sufficient to give a maximum reduction of 25% (1.3 x 10^{-3}M Fe^{+++}). It should be remembered on comparing this with a 25% reduction in 6 hrs. achieved with the apparatus used in Part 1 of this thesis (page 57) that while an 'intermittent' exposure was used there, a continuous exposure is given in the present system.

An aluminium shield was used, of such size as to allow only the irradiation of the iron solution, no direct light reaching the water vapour above it, or the picien joint.

In some instances a Pyrex flask was used instead of a quartz one. This had the effect of cutting down the light intensity and curtailing the spectrum (1 mm. glass removes U.V. below 3100 A°[8]).

The progress of the degassing of distilled water is shown in Table 7.

---

[8] Bowen, 'Chemical Aspects of Light', Oxford University Press, 1947.

mm/

Run	Solution and Conditions	Pressure in ~~M.M.~~ after each freezing. 1st.	2nd.	3rd.	4th.	Pressure after U.V.
1	Distilled Water (Q)	$9\text{x}10^{-2}$	$5.5\text{x}10^{-3}$	$5\text{x}10^{-5}$	-	$1.5\text{x}10^{-3}$
2	Distilled Water (Q)	$7\text{x}10^{-2}$	$5.5\text{x}10^{-3}$	$1.5\text{x}10^{-4}$	-	$2\text{x}10^{-3}$
3	Distilled Water (P)	$6\text{x}10^{-2}$	$1.5\text{x}10^{-3}$	$2\text{x}10^{-4}$	$1.5\text{x}10^{-4}$	$4.5\text{x}10^{-4}$
4	Distilled Water (Q)	$6\text{x}10^{-2}$	$3.7\text{x}10^{-3}$	$6\text{x}10^{-4}$	-	$2.5\text{x}10^{-3}$

TABLE 7.

The Degassing of Distilled Water.

Irradiation flasks - quartz (Q), Pyrex (P).

Irradiation of degassed water in quartz flasks seems to cause formation of a small quantity of gas. That this is not simply a further deaeration was shown by experiments using a Pyrex flask (Run 3). Here a pressure of $\frac{1}{5}$th of that using a quartz flask was obtained. The Pyrex of course cuts off the short ultra-violet light, which may cause a small photo-decomposition of water[9]. Assuming, then, that the gas formed by irradiation is

z/

~~#~~ ll/ [9] Rollefson and Burton, "Photochemistry", New York, 1939, p. 173.

due to a decomposition of the water, the consistency of the results justified an acceptance of a 'blank' pressure of 2×10^{-3} mm. on irradiation of the degassed water in a quartz flask, and the investigation of the iron solutions was begun.

The results, shown in Table 8, give positive experimental evidence that a non-condensible gas is produced on irradiation of ferric chloride solutions under the conditions shown.

TABLE 8.

Degassing of Iron Solutions and Detection of a Photo-Produced Gas.

$[Fe^{+++}] = 1.3 \times 10^{-3}\bar{M}$.

Irradiation Vessels. - Quartz (Q), Pyrex (P).

Solution hydrolysing during irradiation - [H].

Run	Solution and Conditions	pressure after each freezing in m.m.				pp.after irradiation.	% Reduction.
		1st.	2nd.	3rd.	4th.		
5	p_H=3.05, (Q), [H]	1.7×10^{-1}	1.7×10^{-2}	6×10^{-3}		6.0×10^{-2}	22.2
6	p_H=3.05, (Q), [H]	2×10^{-1}	3.2×10^{-2}	6×10^{-3}		4.5×10^{-2}	16.6
7	p_H=3.05, (P), [H].	2×10^{-1}	2.5×10^{-2}	5×10^{-3}	10^{-3}	2.5×10^{-2}	13.0

[cont.over

TABLE 8 (contd.)

$[Fe^{+++}] = 1.3 \times 10^{-3}\overline{M}$.

Irradiation Vessels - Quartz (Q), Pyrex (P).

Solution hydrolysing during irradiation - [H].

Run	Solution and Conditions	Pressure after each freezing in m.m.				pp.after irrad-iation.	% Re-duct-ion.
		1st.	2nd.	3rd.	4th.		
8	$p_H = 3.05$, (Q), [H].	$1.7\text{x}10^{-1}$	$3\text{x}10^{-2}$	$6\text{x}10^{-3}$		$7.5\text{x}10^{-2}$	29.8
9	$p_H = 3.05$, (Q).	$2\text{x}10^{-1}$	$3\text{x}10^{-2}$	$6.5\text{x}10^{-3}$		$2.4\text{x}10^{-2}$	12.0
10	$p_H = 3.05$, (Q), [H].	$2\text{x}10^{-1}$	$2.7\text{x}10^{-2}$	$5\text{x}10^{-3}$		$3.5\text{x}10^{-2}$	17.0
11	$p_H = 3.05$, (Q), [H].	$1.7\text{x}10^{-1}$	$3\text{x}10^{-2}$	$4\text{x}10^{-3}$		$6.5\text{x}10^{-2}$	25.0
12	$p_H = 3.05$, (Q), [H][1]	$1.7\text{x}10^{-1}$	$3\text{x}10^{-2}$	10^{-2}	$1.5\text{x}10^{-4}$	$1.5\text{x}10^{-2}$	6.0
13	$p_H = 2.70$, (Q), [H].	$2\text{x}10^{-1}$	$3\text{x}10^{-2}$	10^{-2}	$4\text{x}10^{-3}$	$3.5\text{x}10^{-2}$	15.8
14	$p_H = 2.70$, (Q).	$1.7\text{x}10^{-1}$	$5\text{x}10^{-2}$	$8\text{x}10^{-3}$	$3.5\text{x}10^{-3}$	$1.3\text{x}10^{-2}$	8.0
15	$p_H = 2.70$, (Q).	$2\text{x}10^{-1}$	$9\text{x}10^{-2}$	$8\text{x}10^{-3}$	$5\text{x}10^{-3}$	$1.2\text{x}10^{-2}$	6.9
16	$p_H = 2.70$, (Q).	$1.7\text{x}10^{-1}$	$4\text{x}10^{-2}$	$8\text{x}10^{-3}$	$4\text{x}10^{-3}$	$1.3\text{x}10^{-2}$	7.0
17	$p_H = 1.80$, (Q).	$2\text{x}10^{-1}$	$5\text{x}10^{-2}$	$4\text{x}10^{-3}$	$4\text{x}10^{-4}$	$4\text{x}10^{-4}$	0.0
18	$p_H = 3.05$, Glucke[2]	$1.7\text{x}10^{-1}$	$9\text{x}10^{-2}$	10^{-2}	$2.5\text{x}10^{-3}$	$2\text{x}10^{-2}$	$>$ 98.0

1. This solution was aged 4 days at 25°C. before irradiation, i.e. Complete hydrolysis had taken place with this treatment.
2. Fe^{+++}/Glucose = 2/1.

The degassing of 'photo-active' iron solutions before irradiation did not seem so effective as with distilled water, e.g. after three freezings the pressure of non-condensible gas above the water had dropped to about 10^{-4} mm. whereas a 'photo-active' iron solution showed a press. $\nless 4 \times 10^{-3}$ mm. and a further freezing made no significant difference. However with a non--photo-active solution, p_H 1.80, (Run 17), a fourth freezing gave a press. of 4×10^{-4} mm. These experiments were conducted in diffuse daylight and although the iron solution was protected from light as much as possible, it appeared that a small photo-reduction was occurring making further degassing difficult beyond 3×10^{-3} mm.

The high vacuum apparatus was transferred to a dark room illuminated by yellow light. No ferrous iron could be detected in iron solutions standing in this light for several days. Nevertheless the same results were obtained.

The solutions at $p_H = 3.05$, i.e. the most photo--active ones, tended to hydrolyse before irradiation. There was a possibility that the colloid might occlude dissolved gases which could make degassing slow. This was tested by ageing a solution of p_H 3.05 for four days at 25°C. after which time hydrolysis was complete. An attempt was then made to degass this fully hydrolysed solution. The degassing proved very successful (Run 12), the press. after four freezings falling to 1.5×10^{-4} mm. It is noteworthy that while such a low pressure was found, the solution was also found to show relatively low photo-activity.

It would thus appear that the difficulty of degassing a solution of high p_H is to be associated with the 'photo-reducibility' of the solution. The inference then is that small amounts of gas are produced by a thermal oxidation of the water by ferric iron. This would suggest that ferrous iron should be produced in amount corresponding to the amount of oxidation of the water, However, no ferrous iron was found. That the analysis was sufficiently sensitive is shown as follows -

After irradiation, a press. of 6×10^{-2} mm.

$= \underline{22.2\% \text{ reduction}}.$

$\therefore$ Before irradiation, a press. of 4×10^{-3} mm.

(taking 'blank' as 4×10^{-4} mm.)

$$= \frac{22.2 \times 3.6 \times 10^{-3}}{6.0 \times 10^{-2}}$$

$= \underline{1.33\% \text{ reduction}}.$

i.e. the 150 ml. of iron solution must have

$$[Fe^{+2}] = 1.3 \times 10^{-3} \times 0.0133$$

$$= 1.73 \times 10^{-5}\bar{M}.$$

This amount is readily detectable by O-phenanthroline (the use of which is described in Part 3 of this thesis).

However, the room-temperature investigation on thermal oxidation did not simulate the degassing conditions, and although there seemed little likelihood of any change during the freezing process the following experiment was carried out in order to verify the absence of a dark reduction. A sample of the iron solution (p_H 3.05) was tested for ferrous ion before degassing - none was found. The degassing cycles were then carried out until after the fourth freezing when the pressure was 6×10^{-3} mm. The flask was then removed and the solution tested for ferrous ion again with a negative result.

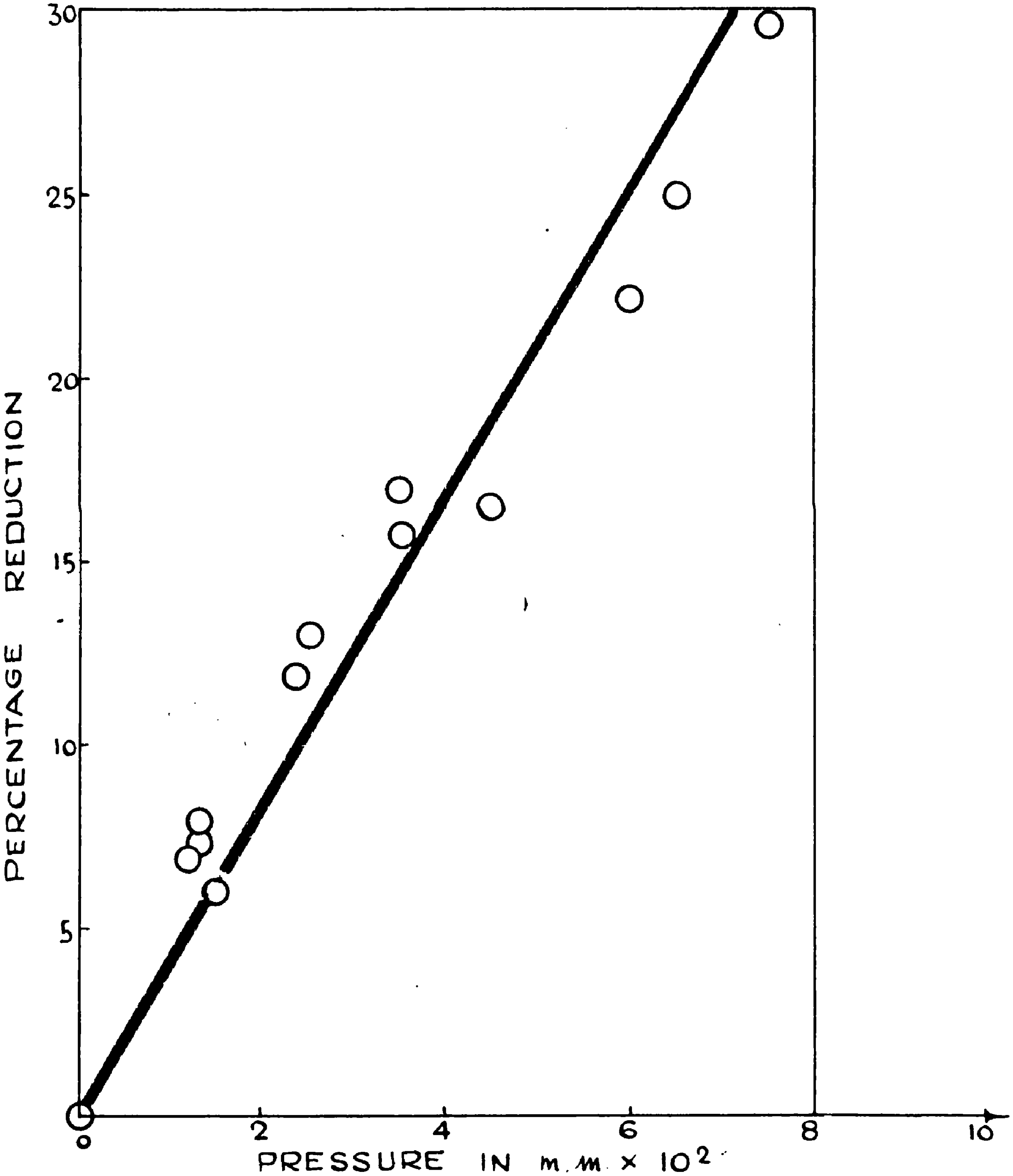
This difficulty of degassing the iron solutions is discussed later.

The magnitude of the pressure after four freezings was sufficiently low to allow of the p.p. after irradiation being considered due to gas produced by the irradiation.

This assumption seemed justified when a plot was made of percentage reduction against press. of gas after irradiation. This is seen to be linear (Fig. 20) as would be expected from a photo-oxidation of the water by ferric iron.

A point to notice is that 'no reduction' corresponded to a press. of 4×10^{-4} mm. (Run 17), i.e. the blank is not 2×10^{-3} mm. as was found with the water (Table 2). This is evidence that exposure of the water alone caused a slight decomposition (already indicated), because with the iron solutions the extinction coefficient of ferric iron in the U.V. is so much higher than that of water, that the decomposition of the water is negligible (experimentally found - pressure 4×10^{-4} mm.).

FIG. 20.



30
25
20
15
10
5
0
2
4
6
8
10
PERCENTAGE REDUCTION
PRESSURE IN m.m × 10²

87

Another feature is that using the substrate glucose (Fe^{+++}/Glucose = 2/1), a reduction of 98.0% ~~reduction~~ was obtained and a pressure of 2×10^{-2} mm. was measured. A possible implication of this result with regard to photo-active species is discussed later.

The variation in reduction shown in Table 8 was achieved by varying the p_H and also the extent of secondary hydrolysis at p_H 3.05 before irradiation (by warming).

To calculate the number of moles of gas evolved, in order that it be compared with that theoretically expected assuming photo-oxidation of the water, the volume of the system must be known. This was measured with the aid of Boyle's Law. With the quartz flask empty, dry air was allowed into the system and the press. measured by the McLeod (0.5 mm.). The flask was then shut off by closing Tap 1. The rest of the system was pumped out to 10^{-5} mm., and tap 4 closed. Opening tap 1 a known volume of air (vol. of flask) at a known pressure (0.5 mm.) was expended into the vacuum of the system, and the final pressure measured on the McLeod. The temperature of the system was room temperature, constant and uniform throughout since the traps were not immersed in liquid oxygen. Thus the volume of the system could be calculated from $P_1V_1 = P_2V_2$.

The number of moles of gas produced on irradiation can be calculated from the ideal gas equation $PV = nRT$.

The volume V is known.

P is the press. of gas in the system. However the press. measured after irradiation was with only one freezing. From the degassing results this is not sufficient to remove <u>all</u> gas but a fairly accurate correction can be made.

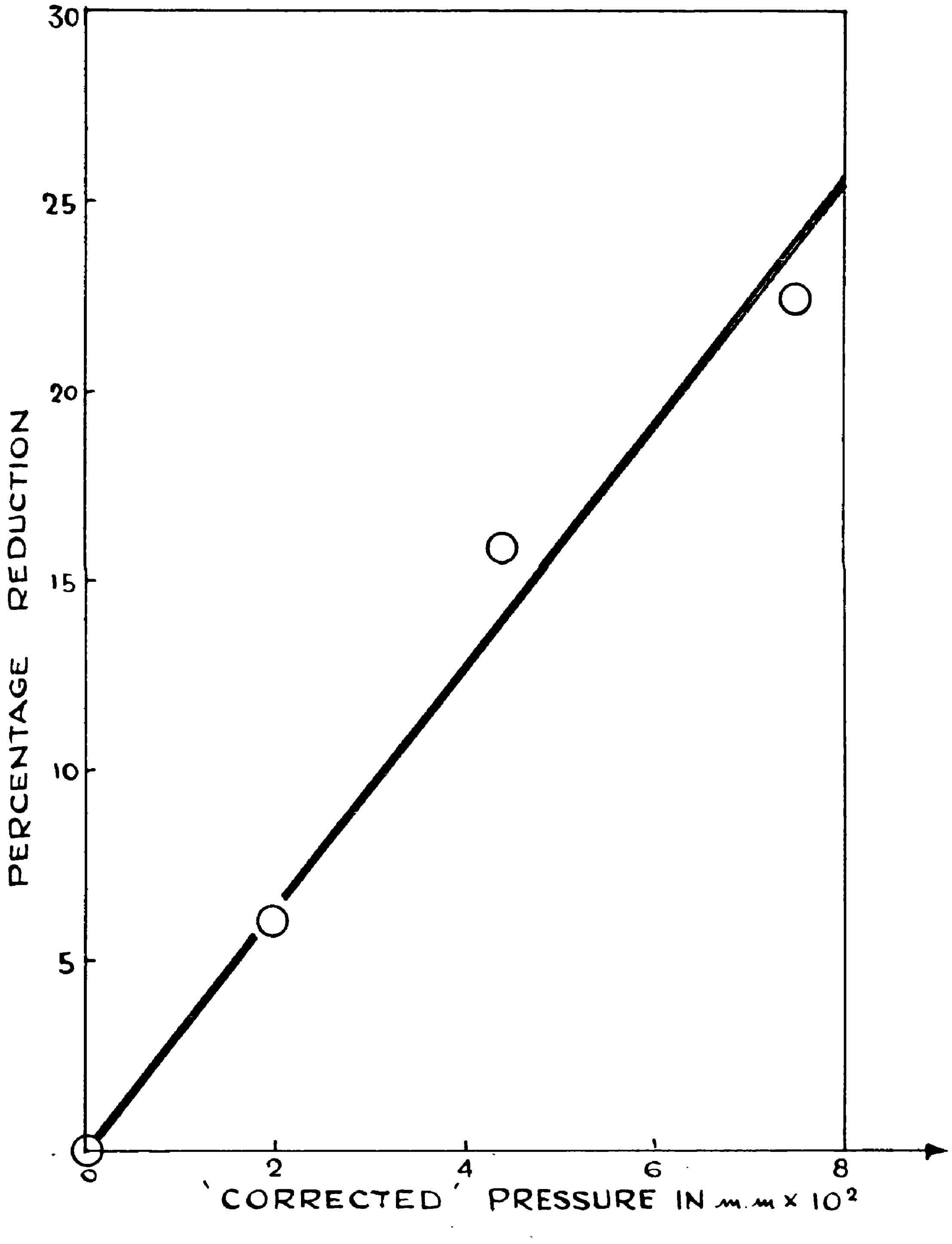
The results of Run 5 are taken for a specimen calculation.

A pressure of 6×10^{-2} mm. was obtained after irradiation with one freezing. A perusal of Table 8 shows that a further second and third freezing would lead to a correction for further gas of 1.0×10^{-2} mm. and 0.5×10^{-2} mm.

i.e. $\bar{p} = (6 + 1.0 + 0.5) \times 10^{-2}$ mm. $= 7.5 \times 10^{-2}$ mm.

This correction was not made for the plot in Fig. 20, but a plot of percentage reduction against 'corrected' press. in Fig. 21 shows that there is no change in the linearity of the function. Four points were taken from Fig. 20 for the corrections which are

FIG. 21.



30
25
20
15
10
5
0
2
4
6
8
PERCENTAGE REDUCTION
'CORRECTED' PRESSURE IN m.m × 10²

shown in Table 9.

TABLE 9.

Corrected Pressures.

% Reduction	Pressure in m.m. after one freezing.	Correction	'True' Press in m.m.
0.0	4×10^{-4}		4×10^{-4}
6.0	1.5×10^{-2}	0.5×10^{-2}.	2×10^{-2}
15.8	3.5×10^{-2}	0.9×10^{-2}	4.4×10^{-2}
22.2	6.0×10^{-2}	$(1 + 0.5) \times 10^{-2}$	7.5×10^{-2}

It must also be considered that the temperature is not uniform throughout the system, since the flask and two traps are immersed in liquid oxygen, and the rest of the apparatus is at room temperature.

For purposes of an approximate calculation the system can be divided into two sections, corresponding to the two different temperatures. The volume of gas immersed in the traps and in the flask was 380 ml. + 100 ml. = 480 ml. and the remaining volume, contained by apparatus at room temperature, was 640 ml.

Section I.	Section II.
$P = 7.5 \times 10^{-2}$	$P = 7.5 \times 10^{-2}$
$V = 480$ ml.	$V = 640$ ml.
$T = -183°C. = 90°K.$	$T = 288°K.$

(There will be a temperature drop across the glass wall of the traps and flask but probably $\ngtr$ 10%).

$P_1V_1 = n_1RT_1$	$P_2V_2 = n_2RT_2$
i.e. $n_1 = \frac{P_1V_1}{RT_1}$	i.e. $n_2 = \frac{P_2V_2}{RT_2}$
$= \frac{7.5 \times 10^{-2} \times 0.48}{760 \times 0.082 \times 90}$	$= \frac{7.5 \times 10^{-2} \times 0.64}{760 \times 0.082 \times 288}$
$= 6.4 \times 10^{-6}$ moles.	$= 2.8 \times 10^{-6}$ moles.

$$\therefore \quad \bar{n} = n_1 + n_2 = 9.2 \times 10^{-6} \text{ moles.}$$

The number of moles of oxygen theoretically expected is calculated thus:-

A 22.2% reduction $= 1.3 \times 10^{-3} \times 0.222$ moles of Fe^{++}/litre

$$= \frac{1.3 \times 10^{-3} \times 0.222 \times 150}{1000} \text{ moles of } Fe^{++}/150\text{ml.}$$

$$= \left(\frac{1.3 \times 10^{-3} \times 0.222 \times 150}{1000}\right) \times \frac{1}{4} \text{ moles } O_2/150\text{ml.}$$

Since the stoichiometry of the equation

$$Fe^{+++} + \tfrac{1}{2}H_2O = Fe^{++} + \tfrac{1}{4}O_2 + H^+$$

shows that 1 mole O_2 = 4 moles of Fe^{++}

i.e. The theoretical no. of moles = $\underline{10.8 \times 10^{-6}}$.

This excellent agreement between the theoretical and experimental amounts of gas from irradiation of the iron solutions, together with the result that the partial pressure of gas formed is a linear function of the ferrous ion produced, is very strong evidence that oxygen is formed by a photo-oxidation of the water by ferric iron.

Absolute identification of the gas was then pursued.

(C). Identification of the Gas by Kautsky's Method.

The silica-gel phosphors (i.e. gel with adsorbed dye) were prepared according to the directions of Pringsheim et al[3,4], except that the aqueous solutions of dye used were more concentrated ($20 \times 10^{-5}\overline{M}$.). This was found necessary as one of the dyes, Uranin, was only feebly adsorbed. This higher concentration is in the range used by Kautsky[1] (5 to $25 \times 10^{-5}\overline{M}$) but the lower molarity was ~~prepared~~ by Pringsheim as

preferred/

the gel seemed to show stronger phosphorescence when prepared under these conditions.

The gel used was 'Purified Silica Gel' from Hopkins and Williams. The average grain size was 0.5 mm. It was ascertained by Pringsheim that the initial purification from iron is carried out with better results by washing the gel for several days with hydrochloric acid and subsequently with distilled water, instead of following Kautsky's method of using sulphuric acid, and after rinsing the gel with water, neutralising with ammonia. The hydrochloric acid used in the present work was of A.R. quality. After a thorough washing the gel was air-dried at room temperature.

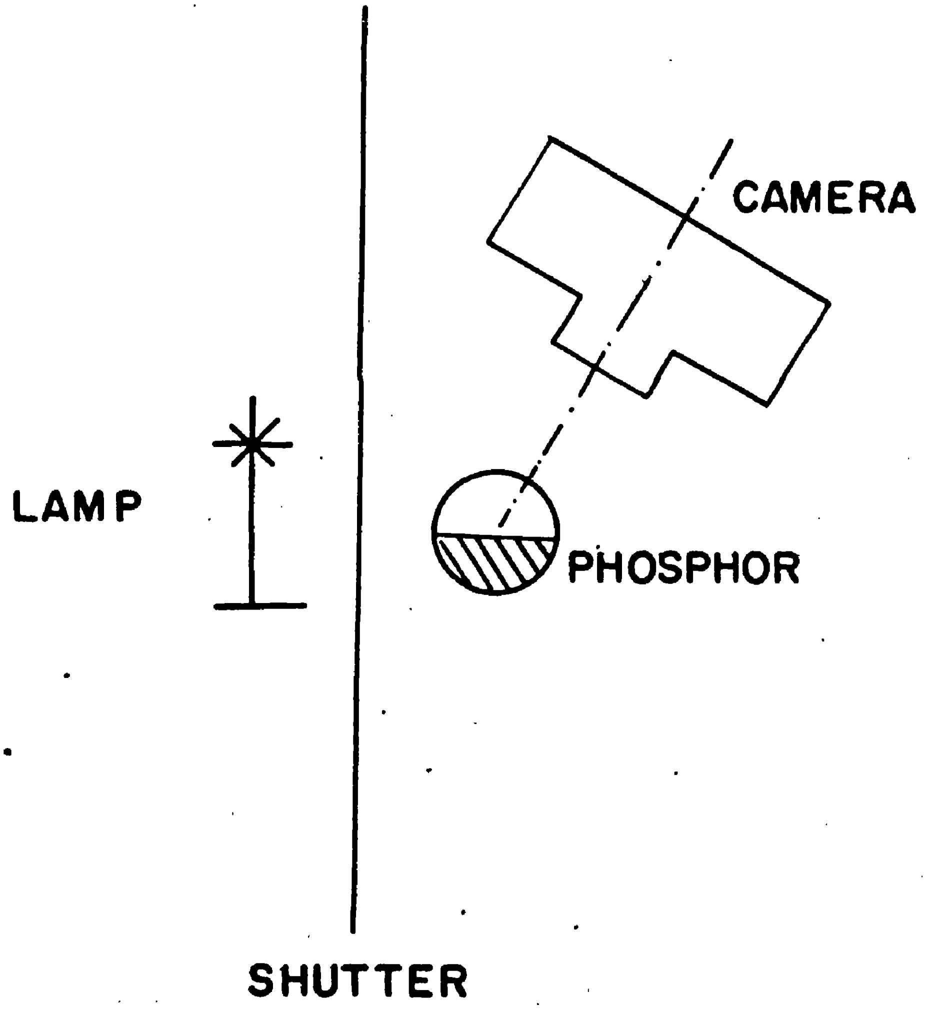
Three different phosphors were prepared from the three dyes Trypaflavine, Uranin (sodium fluorescein) and Euchrysin (Acridine orange). In each case 5 g. of gel were immersed in 50 ml. of a 2 x 10^{-4}M solution of the dye contained in a blackened conical flask, and heated on a steam bath for 8 hours with occasional shaking. The blackened flask was necessary for when the gel, immersed in the dye-stuff solution, is exposed to daylight, many of its grains acquire a brownish colour due to a chemical reaction (oxidation). The dried gel with the adsorbed dye on is much less sensitive to such photochemical influences. However, if an attempt is made to dry the phosphor at 100°C. as above, in presence of air, the grains again turn reddish brown (oxidation). The phosphor, filtered free from dye solution, was thus dried in an oven at 40°C.

After this air-drying the phosphor was introduced into a glass bulb 2 cm. dia and 6 cm. in length, which was then attached to the high vacuum system as shown in Fig. 19. This bulb was evacuated and heated, by means of an oil bath, to 150°C. for 4 hours. This heat treatment was repeated each day the phosphor was in use, although the heating period was cut to 2 hours.

In choosing the most sensitive phosphor, the simple method of measuring the phosphorescence quenching by measuring the time during which the after-glow could be visibly perceived[2], was initially adopted.

The exciting light was the Hanovia S.500 mercury arc lamp and the apparatus (Fig. 22) consisted of this primary light source, an aluminium shutter between the source and the phosphor, and as described later, a

FIG. 22 MEASUREMENT OF PHOSPHORESENCE



wide-aperture camera fitted close to and above the phosphor.

The dark-room that had been used to protect the iron solutions from light became absolutely necessary for this work.

The procedure was that with the shutter up the lamp was switched on for 5 secs., exciting the phosphor. On the 5th second (the seconds were sounded by a metronome) the lamp was switched off, the shutter simultaneously dropped to shield the phosphor from the ebbing light of the lamp, and again simultaneously a stop-watch started. The green afterglow was visibly perceived and timed until it vanished. This vanishing point was fairly sharp. The whole operation required two people and Dr. Good kindly collaborated. Again, since the timing of the afterglow brings in a personal factor, this measurement was occasionally repeated by Dr. Good, our readings agreeing to within 1 sec. with the longest afterglow of 15 secs.

The 5 second excitation by the U.V. lamp was shown to be sufficient to excite the phosphor to its equilibrium, since above this the afterglow did not lengthen.

On investigating the three phosphors it was found that the Uranin phosphor was greatly superior to the other two, both in initial light intensity (visually perceived) and period of afterglow.

The period of afterglow (hereafter called T) of the Uranin under 6×10^{-6} mm. pressure was 15 seconds compared to 5 seconds for the other two.

This difference is probably due to the fact that the Uranin dye was more feebly adsorbed onto the gel in the preparation, which is equivalent to the use of more dilute Trypaflavine solutions suggested by Pringsheim for a stronger phosphorescence.

The Uranin phosphor was thereafter used in all the experiments.

When pure oxygen (supplied by British Oxygen Co.) was allowed into the phosphor bulb (its pressure measured on the McLeod) the phosphorescence was found to be quenched, the amount of quenching being a function of the partial pressure.

This effect was measured by.-

(1) Visual observation of the intensity of phosphorescence immediately after cutting off the light source as described.

(2) Timing the period of afterglow with a stop-watch.

(3) Measurement of the amount of light emitted by the phosphor during its decay by the blackening of an Ilford H.P.S. 35 mm. film in a wide-aperture camera fitted close to the phosphor (Fig. 22).

It was observed by Kautsky and by Pringsheim that water vapour simulated the quenching effect of oxygen. Care was taken to ensure that any water vapour in the present system was condensed by the liquid-oxygen traps.

(1) The effect of oxygen on the initial intensity of phosphorescence as a means of measurement of the gas is most sensitive in the pressure range $10^{-6} - 10^{-3}$ mm.[3] The present measurements of light intensity by eye were purely qualitative. Nevertheless a decrease in light intensity was recognised as the oxygen pressure was increased from 6×10^{-6} mm. in stages to 6×10^{-2} mm. The important range in the present work was 10^{-3} to 10^{-1} mm. These extremes could be clearly distinguished with standard oxygen samples.

It was shown that neither carbon dioxide nor the pure nitrogen used for de-oxygenation of the iron solutions had any quenching effect.

The ferric chloride system was then investigated.

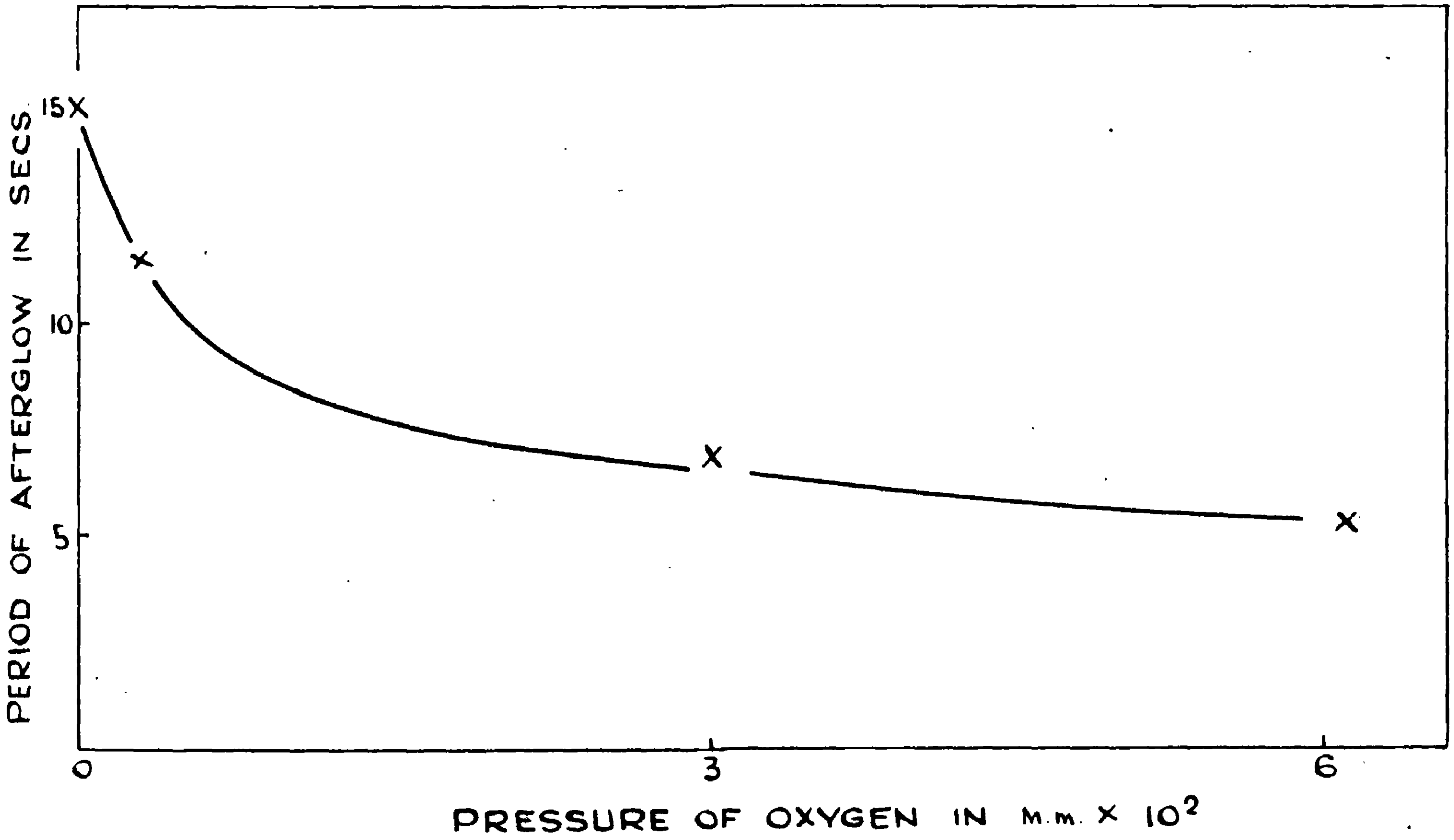
Before irradiation the pressure of non-condensible gas above the solution had dropped to $3\text{x}10^{-3}$mm. by degassing. The effect of this gas on the phosphorescence was tested, and a slight quenching action found, equivalent to a p.p. of about 10^{-3}mm. of pure oxygen. This is discussed later.

On irradiation of the ferric chloride solution a photo-produced gas was detected whose pressure in the system was 6×10^{-2} mm.

The phosphorescence of the gel under high vacuum was noted and the photo-produced gas introduced. Visual observation showed that it had a very marked quenching effect on the intensity of phosphorescence, i.e. the photo-produced gas is oxygen. From experience with standard oxygen samples the degree of quenching was indicative of a pressure of the order 10^{-1} mm. oxygen which compares favourably with the 6×10^{-2} mm. measured.

(2) Fig. 23 indicates the dependence of the period of afterglow (T) on the pressure of standard oxygen samples. It is seen that the sensitivity

FIG. 23. PERIOD OF AFTER GLOW OF PHOSPHORESCENCE AS A FUNCTION OF OXYGEN PRESSURE



of this method sharply decreases with rising oxygen pressure. A minimum afterglow of about 6 secs. is found. This seems to contradict Kautsky's statement that the phosphorescence is completely quenched by oxygen at a pressure of 4×10^{-3} mm. However, Pringsheim et al also question this observation having reported that even in air at atmospheric pressure (150 mm. O_2) phosphorescence was easily visible in all the samples used.

Fortunately, in the present case, there is enough amplitude to distinguish quite clearly between 3×10^{-3} mm. (T = 11.5 secs.) and 3×10^{-2} mm. (T = 7.0 secs.).

With the ferric chloride solution a pressure of 4×10^{-3} mm. (non-condensible gas) was achieved above the solution after three freezings. The phosphor was tested under high vacuum and T = 15 secs. as usual. This pre-irradiation atmosphere was then allowed over the phosphor and the afterglow was shortened to 12 seconds, which is to be expected if the gas is partly oxygen. This is discussed later.

After irradiation and freezing a p.p. of 6×10^{-2} mm.

of non-condensible gas was found. Introducing this into the phosphor shortened the afterglow from 15 to 7 seconds. As with the qualitative observation on diminution of light intensity, this is the result expected of the photo-produced gas was oxygen. The method is not sufficiently sensitive to decide if it is pure oxygen, but this fact was ascertained by sparking with hydrogen as described later.

(3) The 35 mm. camera was used without a lens~~e~~, the wide-aperture being situated within 5 mm. of the phosphor bulb at the angle shown in Fig. 5. The shutter was set at 'time' and controlled by a cable release. The procedure was identical with that for measuring the period of afterglow. After 5 seconds excitation, simultaneously the lamp was switched off, the aluminium shutter dropped, and the camera shutter opened. In the darkness of the room the phosphorescent glow was recorded on an Ilford H.P.S. 35 mm. film with an exposure of 10 seconds, the timing being done by ear from a metronome.

Fig. 24 shows the phosphorescence flux for standard oxygen samples, together with that found

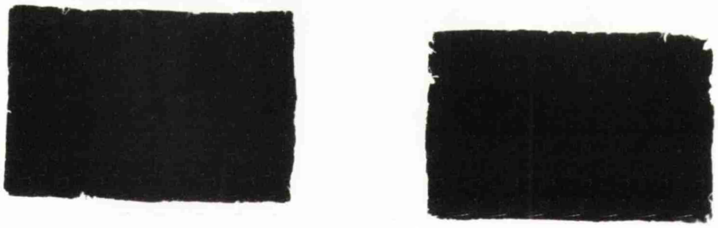
FIG. 24.

10^{-5} m.m.

10^{-3} mm.

10^{-2} mm.

STANDARDS.



BEFORE EXPOSURE

AFTER EXPOSURE

for the gas before and after irradiation.

It was confirmed that the photo-produced gas is oxygen, and that the 'pre-irradiation' gas is partly oxygen too.

(D). Sparking of the Gas with Hydrogen.

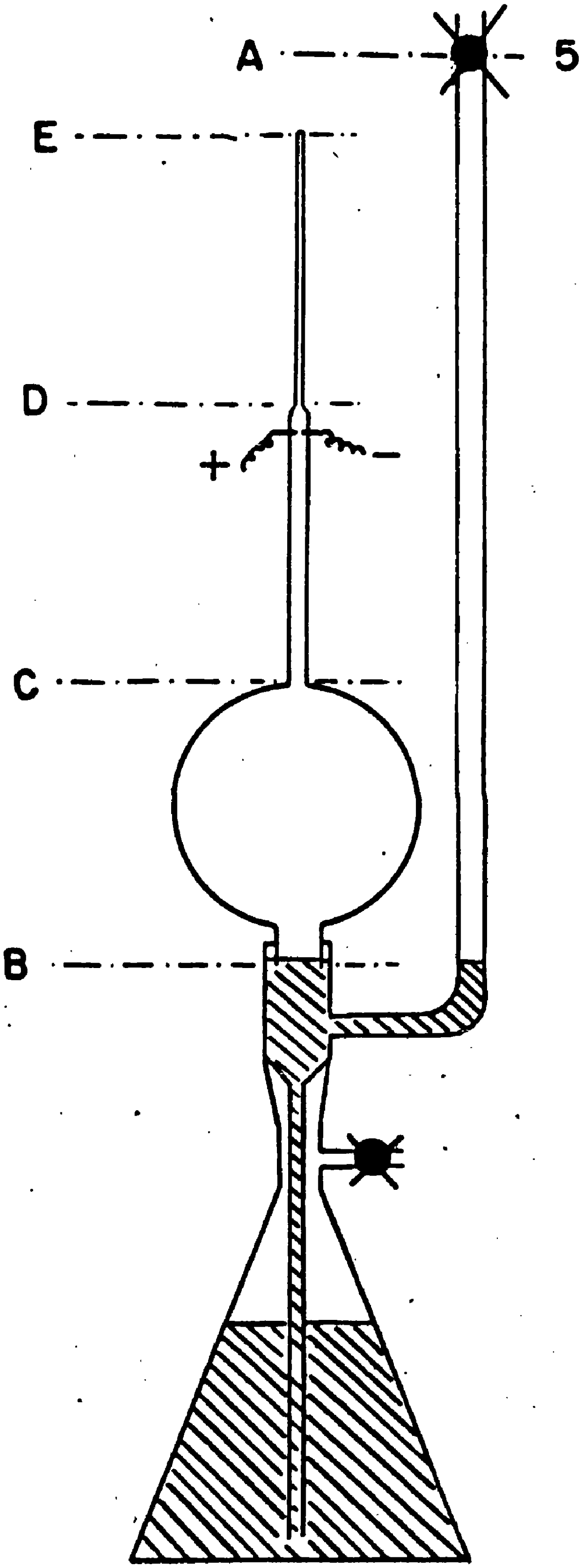
As confirmation that the photo-produced gas was oxygen it was sparked with hydrogen in a micro gas-pipette. This was a modified McLeod gauge, platinum electrodes being inserted first below the capillary. The platinum glass seals were made vac-tight with the aid of picien wax. The apparatus is shown in Fig. 25.

The procedure was as follows:-

After irradiation, the photo-produced gas was frozen out of solution as usual. With the system under high vacuum (6×10^{-6} mm.) tap 4 was closed and tap 1 opened allowing the non-condensible gas to permeate through the system, and the pressure measured on the Mcleod.

Tap 5 was then opened and the gas expanded into the sparking apparatus. The mercury was raised to just below level B (Fig. 25) and the pressure of gas measured on the Mcleod. Thereafter the mercury was raised above B and a portion of gas was cut off in the

FIG. 25. SPARKING APPARATUS FOR GAS ANALYSIS



bulb. The volumes between B and C, C and D, D and E, were accurately known (etched on the bulb by the makers and also measured by expansion technique as for volume of vacuum system). The introduction of the electrodes made a negligible difference to the volume.

Thus a portion of gas was trapped of known pressure (measured on the Mcleod) and known volume (B to E).

This having been done, the whole system was again put under 6 x 10^{-6} mm. pressure up to B.

Meanwhile a gas pipette had been filled with pure hydrogen, from a cylinder, and attached to the vacuum system as shown (Fig. 19), a high vacuum being present up to tap 7.

By closing tap 8 (i.e. pumps cut off) and tap 3 (to decrease the volume of the system), tap 7 was opened and pure hydrogen permeated through the system as far as B in the explosion apparatus. The pressure of hydrogen was measured on the Mcleod.

This pressure was higher than required and by carefully pumping a little hydrogen away at a time, the pressure was adjusted to such a value that when tap 5 was closed (sealing off the volume of hydrogen between A and B) and the level of mercury lowered below B to allow the gases to mix; the partial pressure ratio of $H_2/\text{Gas} = 2/1$. This necessitated knowing the volume between A and the level at B, which was accurately measured. Due to the difficulty of pumping away a desired amount of hydrogen the correct ratio of 2/1 was not easy to obtain, but with experience appropriate amounts of hydrogen were isolated, the final mixture ration being accurately known.

The gas mixture was then compressed into the capillary and sparked. The spark was obtained from an induction coil with a feed of 4 volts in the primary.

A decrease in volume showed that combination had taken place. It was demonstrated that hydrogen did not combine with nitrogen under these conditions.

The results of two separate experiments are given below. The photo-produced gas is termed G.

Experiment I.

Volume between A and level at B = V_1 = 80 ml.

Volume between level at B and 0 = V_2 = 160 ml.

(a) The photo produced gas was allowed into the sparking apparatus and a portion trapped by raising the mercury to B.

i.e. $V = V_2 = 160$ ml. from $pV = nRT$

$p = 7.5 \times 10^{-2}$ mm. $n = \frac{7.5 \times 10^{-2} \times 0.16}{760 \times 0.082 \times 293}$

$= 6.55 \times 10^{-7}$ moles.

∴ 6.55×10^{-7} moles of G are trapped in the bulb.

(b) A pressure of 0.18 mm. of hydrogen was allowed into the sparking apparatus as far as level B and tap 5 closed.

i.e. $V = V_1 = 80$ ml. $n = \frac{PV}{RT} = \frac{0.18 \times 0.08}{760 \times 0.082 \times 293}$

$= 7.85 \times 10^{-7}$ moles.

∴ 7.85×10^{-7} moles of H_2 trapped in limb AB.

(c) The level of the mercury was lowered below B and the gases allowed to mix.

The mercury was then raised to level B again cutting off 160 ml. of gas mixture, i.e. $6.55 \times 10^{-7} \times \frac{160}{240} = 4.36 \times 10^{-7}$ moles of G.

and $7.85 \times 10^{-7} \times \frac{160}{240} = 5.24 \times 10^{-7}$ moles of H_2.

(d) This mixture was compressed into the capillary and sparked. The sparking was continued until there was no further decrease in volume.

After combination the volume of the remaining gas was calculated knowing the volume of the whole length of the capillary and assuming it to be of uniform bore.

The pressure was measured by the difference in heights between the mercury in the capillary and the mercury in the adjoining limb of this modified Mcleod.

$V = 0.059$ ml. $\therefore n = \frac{PV}{RT} = \frac{55 \times 0.059 \times 10^{-3}}{760 \times 0.082 \times 293}$

$p = 55$ mm.

$= 1.78 \times 10^{-7}$ moles.

$\therefore$ Gas remaining after combination $= 1.78 \times 10^{-7}$ moles.

The previous work has indicated that G is oxygen. If this is so, the stoichiometric quantity required, i.e. the gas remaining after sparking is G.

$\therefore$ initial G $= 4.36 \times 10^{-7}$ moles. $\therefore$ 2.58×10^{-7} moles

final G $= 1.78 \times 10^{-7}$ moles of G have combined

with H_2.

i.e. 5.24×10^{-7} moles of H_2 have combined with 2.58×10^{-7} moles of G.

$\therefore$ Combination ratio $= \frac{5.24}{2.88} = \frac{2.03}{1}$.

Experiment II.

The details of the sequences are as in I.

(a) 7.65×10^{-7} moles of G are trapped in the bulb.

(b) 11.55×10^{-7} moles of H_2 are trapped in side limb.

(c) Explosion mixture is 5.1×10^{-7} moles of G.
8.65×10^{-7} moles of H_2.

(d) Gas remaining after combination = 1.05×10^{-7} moles.

∴ initial G = 5.1×10^{-7} moles. 4.05 moles of G
final G = 1.05×10^{-7} moles. reacted $\times 10^{-7}$.

∴ 8.65×10^{-7} moles of H_2 have combined with
4.05×10^{-7} moles G.

∴ Combination ratio $= \frac{8.65}{4.05} = \frac{2.14}{1}$

It may therefore be assumed that the photo-produced gas from the irradiation of the ferric chloride solutions is pure oxygen.

Discussion.

Since no chlorine was detected it would appear that if the reaction

$$OH + Cl^{-} \longrightarrow OH^{-} + Cl$$

does occur, the Cl is removed by the oxidation of Fe^{+2}

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

The difficulty of degassing iron solutions of high p_H as compared with water is rather puzzling. It could be attributed to a difference in crystal habit on freezing, the solid iron solution retaining dissolved gases more readily than water. However degassing is less easy as the p_H is raised from 2.0 to 3.0, but it may simply be fortuitous that a change in crystal habit of the frozen iron solution takes place in this p_H range, the higher the p_H the more retention of gases. That part of this gas is oxygen is very puzzling.

It was established that a correlation between ease of degassing and photo-activity of the solution though feasible holds no ground experimentally, i.e. no small photo- or thermal oxidation of the water by ferric ion takes place.

Whatever the reason, the gas evolved after irradiation is due solely to the action of light on the iron solution and is in amount 10 to 20 times greater, than that expected if it were simply due to a further 'degassing'.

The pressure of the photo-produced gas evolved is a linear function of the ferrous ion produced and moreover its absolute magnitude is in accordance with the stoichiometry of the equation

$$Fe^{+3} + \tfrac{1}{2}H_2O = Fe^{+2} + \tfrac{1}{4}O_2 + H^+$$

The gas was shown to be oxygen by the phosphor technique of Kautsky and also by sparking with hydrogen.

The photo-oxidation of water by ferric ion is thus established.

The experimental results may be explained by at least two mechanisms.

(1). $\underline{\text{The Initial Step } Fe_2(OH)_2^{+4} \xrightarrow{h\nu} Fe^{+2} + OH + Fe^{3+}OH^-}$.

followed by back reaction

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

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

$$OH + OH \longrightarrow H_2O_2$$

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

$$Fe_2(OH)_2^{+4} + OH \longrightarrow \underset{Fe^{+3} + Fe^{+}}{\cancel{2Fe^{+2}}} + OH^- + H_2O_2$$

The hydrogen peroxide will decompose either by

(a) Back oxidation of Fe^{+2}

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

(b) By reaction with Ferric

e.g. $Fe^{+3}OH^- + HO_2^- \longrightarrow Fe^{+2} + OH^- + HO_2$

$$HO_2 \longrightarrow H^+ + O_2^-$$

$$Fe^{+3}OH^- + O_2^- \longrightarrow Fe^{+2} + OH^- + O_2$$

or $Fe^{+3} + O_2^- \longrightarrow Fe^{+2} + O_2$

(2). The Initial Step $Fe_2(OH)_2^{+4} \xrightarrow{h\nu} 2Fe^{+2} + H_2O_2$.

Then, the hydrogen peroxide decomposes as in (1) Uri suggested that the two competing reactions in the photo-oxidation of water by ferric ion would be

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

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

and concludes that in view of the considerably lower ionisation potential of the Fe^{+2} in aqueous solution (in comparison with the ceric cerous system) the ratio k_o/k_i will be very large, and that therefore extremely high light intensities and large $Fe^{+3}OH^{-}$ concentrations would be required to obtain measurable oxygen yields.

These conditions would not have to be so drastic if the "dimer" decomposes intramolecularly as suggested above. It should however by noted (Table 5 page 86) that at p_H 3.05, before secondary hydrolysis, $Fe^{+3}OH^{-}$ and "dimer" form about 36% and 25% respectively of the total iron in solution, and that the light source, an unfiltered 500 watt U.V. lamp at a distance of 8 cm., provides quite a high intensity.

When an iron-glucose system of concentration ratio 2/1 was irradiated(Run 18. Table 8), the reduction of the iron was > 98%, but a gas was detected, pressure 2×10^{-2} mm., i.e. equivalent to ~10% reduction of the iron. This gas could be attributed to an intramolecular decomposition of the "dimer" to Fe^{+2} and H_2O_2, and the peroxide decomposes to oxygen. The formation of H_2O_2 would be independent of substrate concentration.

i/ On the other hand ~~o~~f H_2O_2 formation is achieved by

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

then the substrate glucose would provide a very strong competing reaction

$$\text{Glucose} + OH \longrightarrow \text{Products}$$

and no gas would be expected.

However, considering all the reactions which are thermodynamically possible in this system, a complete kinetic analysis is impossible and only tentative suggestions can be made as to the individual reaction steps.

That colloidal ferric hydroxide plays a major part in the scheme is evident from the increase in photo-activity of the solution on secondary hydrolysis. This is discussed later in Part 4.

A preliminary study with monochromatic light was initiated and is described in Part 3.

PART 3.

A PRELIMINARY KINETIC STUDY.

Introduction.

It is considered that for a thorough investigation of this photochemical reaction the kinetics of ferrous ion formation would have to be followed in conjunction with oxygen evolution. This could be done most readily by the method of Franck and Pringsheim(described on page 95, Part 2). Preparations are being made in this laboratory for an investigation of this kind.

The work reported here is preliminary to the investigation envisaged and the kinetic results are based only on ferrous ion formation. The principle aim was the measurement of the quantum yield.

The light input was measured by chemical actinometry. The uranyl oxalate actinometer has been the one most widely used in recent years.

For large doses of radiation it has important advantages[1,2,3], and at short wavelengths its sensitivity can be increased by the use of dilute solutions[4] but

---

[1] Leighton and Forbes, J.A.C.S., 1930, 52, 3139.

[2] Heidt and Daniels, J.A.C.S., 1932, 54, 2384.

[3] Brackett and Forbes, J.A.C.S., 1933, 55, 4459.

[4] Forbes and Weidt, J.A.C.S., 1934, 56, 2363.

it is unsuitable for low light intensities owing to the difficulty of measuring accurately the small difference between two titrations.

A new sensitive chemical actinometer has recently been developed by Parker[5]. This depends on the photo--decomposition of the ferroxalate ion according to the equation

i/

$$2[Fe(C_2O_4)_3]^{3-} \longrightarrow 2Fe(C_2O_4) + 3(C_2O_4)^{2-} + 2CO_2$$

Most of the measurements were made on a solution of 0.006 $\bar{M}$ potassium ferrioxalate in 0.1$\bar{N}$ sulphuric acid. In this system the photolysis products absorb weakly (i.e. no disturbance of the linearity of response due to inner filters) and one of them, ferrous ion, can be readily transformed into a strongly absorbing substance by subsequent reaction with o-phenanthroline and thereafter accurately analysed by spectrophotometry. The complex of o-phenanthroline with ferrous ion is more stable than that with ferric iron (Lea, Kolthoff and Leussing[6]) and has a strong absorption band with peak intensity at a wavelength of 5100A°. where the absorption by the ferrioxalate ion if very low.

---

[5] Parker, Proc.Roy.Soc., 1953, Series A, 220, 104.

[6] Lea, Kolthoff and Leussing, J.A.C.S., 1948, 70, 2348.

According to Parker the ferrioxalate actinometer offers the following advantages:-

(1) Sensitivity.

The minimum detectable amount of energy is of the order 5×10^{-10} N quanta. Energies greater than 100 times this quantity can be determined with an accuracy of ± 2%. It is thus some hundreds of times more sensitive than the uranyl oxalate actinometer. It may therefore by used to advantage for the investigation of weak monochromatic sources such as the exit slit of a narrow aperture monochrometer, no unduly long exposure being required. Parker also suggests that it may prove to be useful in the evaluation of high intensity flashes of short duration by enabling accurate determinations to be made over selected narrow bands of wavelength.

(2) Wave-lengths covered.

The quantum efficiency gradually increases from about 0.9 to 1.2 as the wave-length drops from 4,800 A°. to 2537A°. This gradual and comparatively small change in quantum efficiency makes the actinometer very suitable for polychromatic photometry. With the most concentrated solutions light absorption is substantially complete (1 cm. thickness) at 4358 A°. and remains sufficiently high for convenient use up to about 4800 A°. Results indicate that satisfactory working conditions could be obtained at wave-lengths down to 2,000 A°.

(3) Stability of photolyte and photolysis products.

The actinometer solution can be kept for long periods of time if storred in the dark. Even in the presence of air photolysis products show a negligible decomposition in 24 hours. Oxygen has no effect on the quantum efficiency at 3650 A°.

(4) Simplicity of Operation.

The analytical procedure of absorption spectrophotometry is very simple and a large number of determinations can be made in a short time. The quantum yield at 3650 A°. remains constant when the degree of decomposition is varied by a factor of nearly 3,000. Although stirring is desirable for the most precise work its absence leads to little change in the quantum efficiency at least at the longer wavelengths.

The potassium ferrioxalate actinometer was used in the present investigation.

Experimental.

Laboratory lighting.

Because of its high sensitivity the actinometer solution cannot be used in a daylight-filled laboratory. All work was carried out in a dark room illuminated by Kodak OB safelights (lime-yellow). This precaution is also of some value when studying ferric chloride solutions.

Materials.

The materials for the photo-reduction of ferric chloride were as described before (Part I).

Solid potassium ferrioxalate was prepared by mixing 3 volumes of 1.5 $\bar{M}$ A.R. potassium oxalate with 1 volume of 1.5 $\bar{M}$ A.R. ferric chloride stirring vigorously. The precipitate (green crystals) was recrystallised four times from hot water and dried overnight in an oven at 45°C. The whole procedure was carried out in the dark room. Estimation of oxalate (with permanganate) and iron (with titanous chloride) gave respectively 101.3 and 101.1% calculated as $K_3Fe(C_2O_4)_3.3H_2O$ (c.f. Parker, 100.6 and 100.8% respectively). The actinometer solution was prepared by dissolving the solid in 0.1$\bar{N}$ sulphuric acid.

Optical Arrangement.

The apparatus is shown in Fig. 25A. The light source used was a 250 W.M.E. D. mercury vapour lamp supplied by G.E.C. complete with control unit consisting of a choke and condenser through which the lamp was connected to the mains. The lamp gave a steady output for long periods of time. Another advantage was the small size of the arc, 3.75 mm., which made it relatively easy to produce a nearly parallel beam by means of a quartz condensor lens of 6.5 cm. focal length. The emergent parallel beam then passed through filters for the isolation of spectral regions.

3650-3663 gp. of lines:- 2 cm. of copper sulphate solution (125 g. of $CuSO_4.5H_2O$ made up to 1 litre with water) in conjunction with 2 mm. of chance glass OX 1[7].

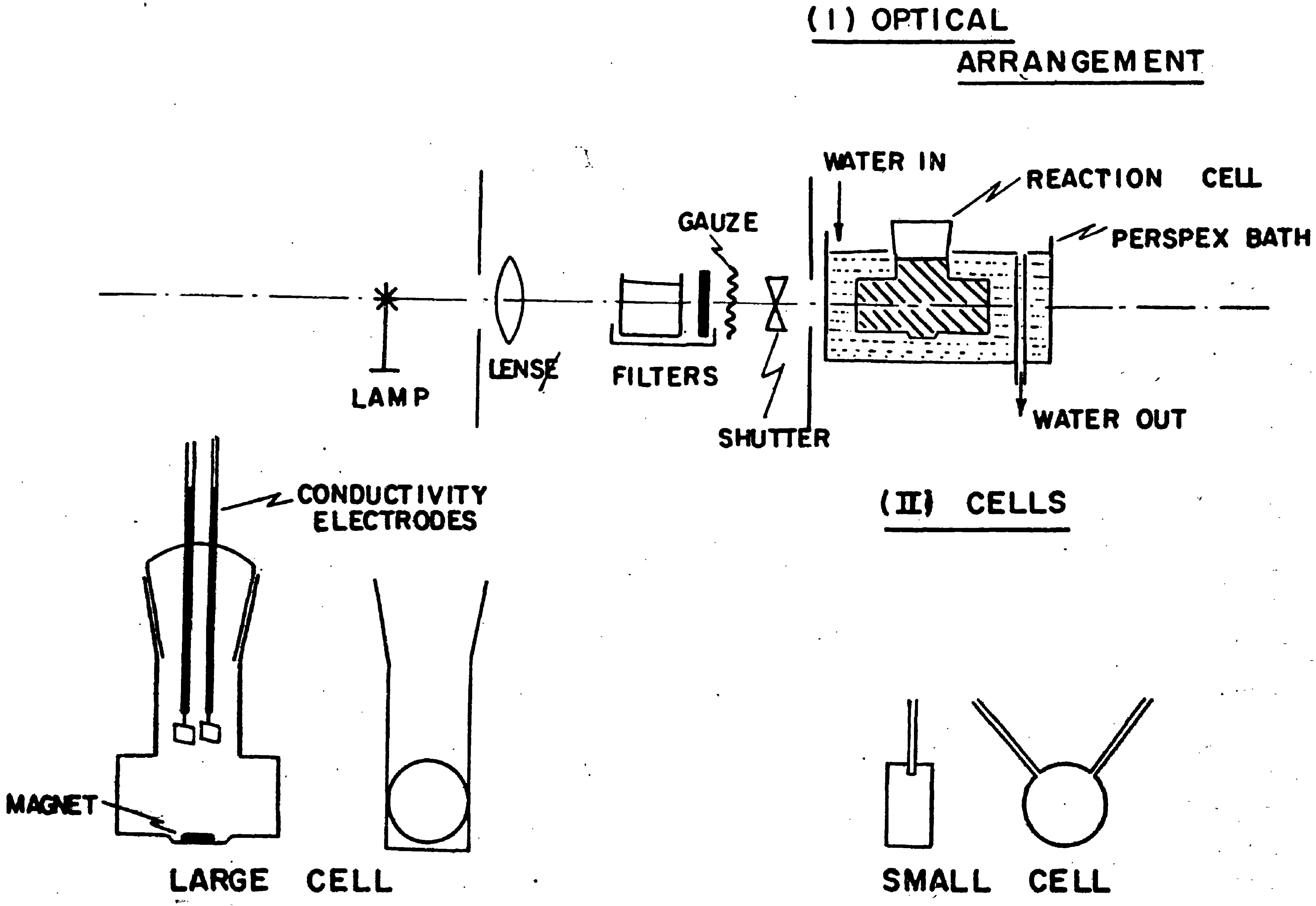
$\geq$ 4200 A°., 0.5 cm. of saturated sodium nitrite[7].

Once through the filters the beam fell onto a shutter. This was a 'Pronto' camera shutter and could be opened and closed by cable release. It was a necessary piece of equipment when timing exposures whose duration was

---

[7] Bowen, 'The Chemical Aspects of Light', Oxford University Press.

FIG. 25A. PHOTOCHEMICAL APPARATUS



in seconds.

The light emerging from the shutter passed through the quartz window of a perspex box of dimensions (15 cm. x 12 cm. x 11 cm.) in which the reaction vessel was clamped in position. The larger quartz cell was magnetically stirred, a magnetic stirrer being permanently fixed onto the underside of the perspex box, as shown.

This whole arrangement was mounted on an optical bench over a large thermostat bath. Water was pumped up from the bath to the perspex box which had a constant level device and this, circulating water kept the irradiated solutions at a constant temperature. This was not so important for actinometery but was very necessary with the ferric chloride solutions as the formation of ferric hydroxide is very sensitive to temperature change.

Reaction Cells.

A Two cells were used and are shown in Fig. 25. The larger one had optically plane face ~~focus~~ of 4 cm. diameter and an optical depth of 7 cm. Volume of solution taken was 150 ml. It is noted that it had a 'seat' for the magnetic stirrer (a small magnet enclosed in glass) and a B.40 socket top. A 'dip-type' conduction cell was fitted in as shown. The cell was pure quartz made to our specifications by Q.V.S. limited.

The smaller cell was constructed by fixing two quartz end-pieces onto a 2 cm. cylinder of large bore glass tubing by means of 'Araldite' 103, a potent cold-setting resin used with a hardner. The cell was of diameter 4 cm. optical depth 2 cm. and volume 19.7 ml.

Both cells were used for irradiation of ferric chloride solutions and the smaller one was also used for actinometry.

Variation of Light Intensity.

A decrease in light intensity was achieved by means of wire gauzes placed between the reaction cell and the filters. No pattern was obtained on paper placed in the position of the reaction vessel.

Reaction Technique.

The photo-reduction of ferric chloride was carried out in two ways.

(a) Using the large cell the reaction was followed by pipetting out 2 ml. samples at noted time intervals and analysing the ferrous ion produced by o-phenanthroline. The initial volume of 150 ml. was not greatly changed as only about 8 samples were taken over a run. The decrease in volume of the solution with time was of course considered when calculating the number of moles of ferrous ion formed. The solution was stirred by a magnetic stirrer.

(b) The small cell was filled with iron solution and irradiated for a measured time interval. The solution was not stirred. The whole content of the cell was then used for analysis.

It was found necessary to use method (1) for an accurate estimate of the initial rate of ferrous ion formation to calculate the quantum yield.

Measurement of Secondary Hydrolysis.

The hydrolysis of ferric iron to ferric hydroxide was followed (in conjunction with the photo-reduction) by conduction measurements using the 'dip-cell' shown in Fig. 25A. This method was used by Lamb and Jacques[8].

Fig. 26 compares the detection of hydrolysis by conduction and by colour formation (the latter method is described in Part I). Good agreement was achieved.

Actinometry.

The ratio

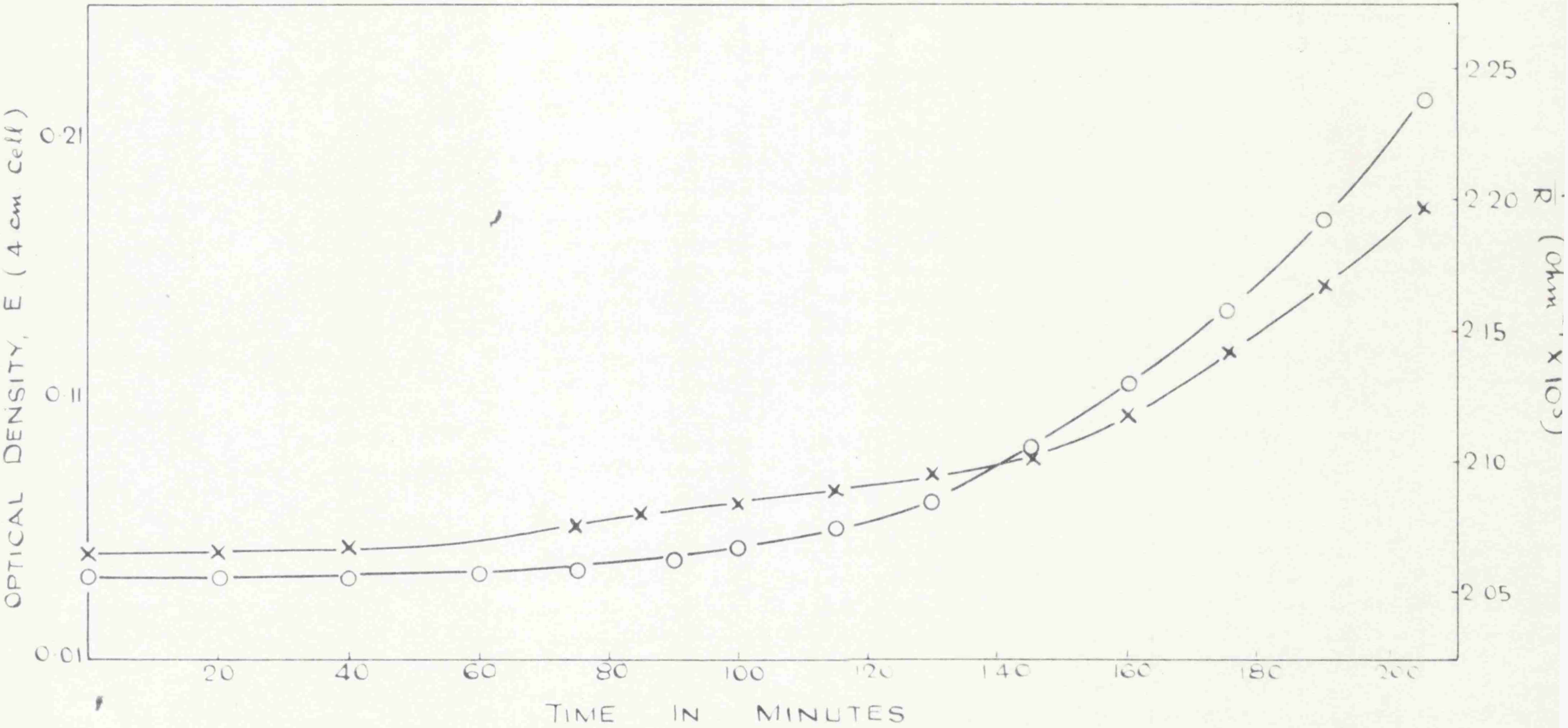
$$\left[\frac{\text{chemical change in gm. mols. for time t}}{\text{light energy absorbed in time t}}\right] \text{ for a}$$

---

[8] Lamb and Jacques, J.A.C.S., 1938.

FIG 26. APPEARANCE OF SECONDARY HYDROLYSIS AS SHOWN BY CONDUCTIVITY AND COLOUR FORMATION

X, CONDUCTIVITY O, OPTICAL DENSITY



photochemical reaction is termed the quantum yield (γ). Light energy is expressed in $Nh\nu$ units or Einsteins where N = avogadros constant, h = Planck's constant, ν = frequency, of absorbed radiation.

Then $\gamma = \frac{d\,Fe^{++}/dt}{k\,I}$ where k = light absorption fraction
I = energy impact in Einsteins per unit time.

With a path length of 2 cm. of ferrioxalate solution there is total absorption up to about 70% decomposition, i.e. k = 1.

$$\therefore \quad \gamma = \frac{d\,Fe^{++}/dt}{I}$$

$$\therefore \quad I = \frac{d\,Fe^{++}/dt}{\gamma}$$

Analysis of Ferrous ion by o-Phenanthroline.

The equilibrium

$$H^{+} + Fe(C_{12}H_8N_2)_3^{++} \rightleftharpoons Fe(C_{12}H_8N_2) + C_{12}H_8N_2^{+}$$

lies increasingly to the right **below** p_H 3.0. It is clear from the equilibrium that for ~~qual~~quantitative complex formation excess o-phenanthroline is necessary.

Lea, Kolthoff and Laussing[6] have calculated that the ratio of excess o-phenthroline to H^{+} should be 0.035 or greater.

The procedure worked out by Parker for his actinometry was adopted for exposed ferrioxalate solutions.

Up to 10 ml. of photolysed solution (0.1 $\bar{N}$ sulphuric acid) was transferred to a 20 ml. calibrated flask. 2 ml. of a 1:10 o-phenanthroline solution (0.1% of monohydrate in water) was added followed by a volume of buffer solution (600 ml. of $\bar{N}$ sodium acetate + 360 ml. of $\bar{N}$ sulphuric acid made up to 1 litre) equal to half the volume of photolyte taken. This buffer was chosen to produce a <u>final p_H value of 3.5</u>.

After making up and mixing, Parker allowed the liquid to stand for ½ hour to allow complete reaction and then its absorption at 5100 A°. was measured on ~~our~~ a X.P.500 spectrophotometer. (The colour was found to be stable for 24 hr. at least).

In the present work colour formation was found to be very slow and it took much longer than ½ hour before the maximum value was reached. However on addition of 1 ml. of saturated ammonium fluoride solution (<u>after</u> the other reactants were in the flask) the maximum colour was achieved almost instantaneously.

This was also found by Baxendale and Bridges[9] who attributed the action of F^- in accelerating colour formation to the complexing of the ferric ion. However, the present investigation showed this explanation to be wrong since it was found that F^- accelerates colour formation of the ferrous complex when no ferric ion is present (using ferrous ammonium sulphate). It would appear that the action of F^- is directly catalytic and not simply complexing. The colour is stable for only 15 minutes with ferrioxalate solutions and then begins to deepen (a reduction of $Fe^{+++} \longrightarrow Fe^{++}$? This question was not pursued). The order of addition of reagents was found to be critical. It was

Fe^{+2} + o-phenanthroline + buffer + F^-

made up to 20 ml. The colour was measured by absorption at 5100 Å., with a Unicam S.P. 250 spectrophotometer.

Linear calibration graphs were obtained, using A.R. ferrous ammonium sulphate, up to 1.0 extinction with 4 cm. and 1 cm. cells. The appropriate 'blank' correction was of course applied in all determinations (with potassium ferrioxalate this was 0.004 with a

---

[9] Baxendale and Bridges.

1 cm. cell). The photolyte was found to be stable if stored in the dark. An extinction of 0.552 in a 1 cm. cell was produced by a concentration of $5 \times 10^{-5}\overline{M}$ ferrous ion, corresponding to a molecular extinction coefficient of 11040 for the complex. This agrees well with Parker's result of 11050 by the same method and 11100 found by Smith, McCurdy and Diehl[10] by the more convential procedure.

The ferrous ion produced by the photo-reduction of ferric chloride solutions was measured in the same way. Reduction values at the stationary level were confirmed by titration with titanous chloride solution.

---

[10] Smith, McCurdy and Dhiel, *Analyst*, 1952, *77*, 418.

Results.

A. Actinometry.

The 'standard' actinometer solution, 0.006 M potassium ferrioxalate in 0.1 N sulphuric acid, was exposed to light of 3$\overset{6}{\cancel{8}}$5 mμ at 20°C. in the 2 cm. cell. The exposure was timed with a stop watch (1 rev. = 10 secs.). Fig. 27 shows the ~~limit~~ time-average rate of ferrous ion formation with increasing exposure time. The decrease in $d\,Fe^{+2}/dt$ after 2 minutes was due to incomplete absorption of the light through lack of stirring. For measurements of light intensity a 1 minute exposure was adopted.

A specimen measurement is shown below.

Volume of solution = 19.4 ml. Exposure = 62.7 secs.

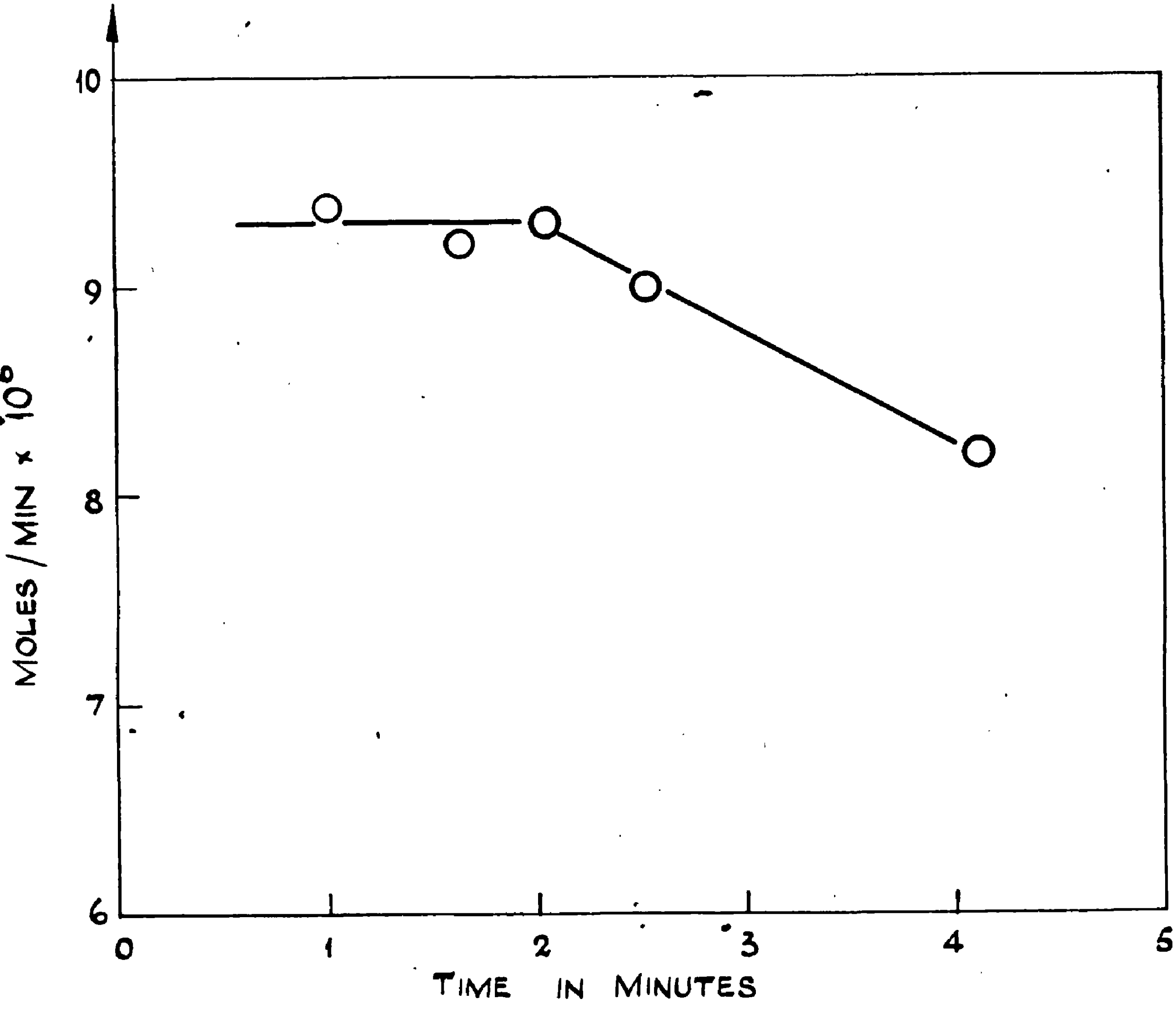
By analysis with o-phenthroline the ferrous ion produced = = 5×10^{-4} M.

$$\therefore \text{ No. of moles of } Fe^{+2} \text{ produced} = \frac{5\times10^{-4}}{1000} \times 19.4$$

$$= 9.\overset{7}{\cancel{8}}0 \times 10^{-6}$$

$$\therefore \frac{d\,Fe^{+2}}{dt} = 9.\overset{7}{\cancel{8}}0 \times 10^{-6} \times \frac{60}{62.7} = 9.\overset{3}{\cancel{4}} \times 10^{-6} \text{ moles/min.}$$

FIG 27. FERRI-OXALATE ACTINOMETER
TIME - AVERAGE RATE OF FERROUS-IRON FORMATION WITH DURATION OF EXPOSURE



$$\text{but } I = \frac{d\,Fe^{+2}/dt}{\gamma}$$

Parker's value for γ at 365 mu is 1.18

$$\therefore \quad I = \frac{9.4 \times 10^{-6}}{1.18} = 8 \times 10^{-6}\ Nh\nu/\text{min.}$$

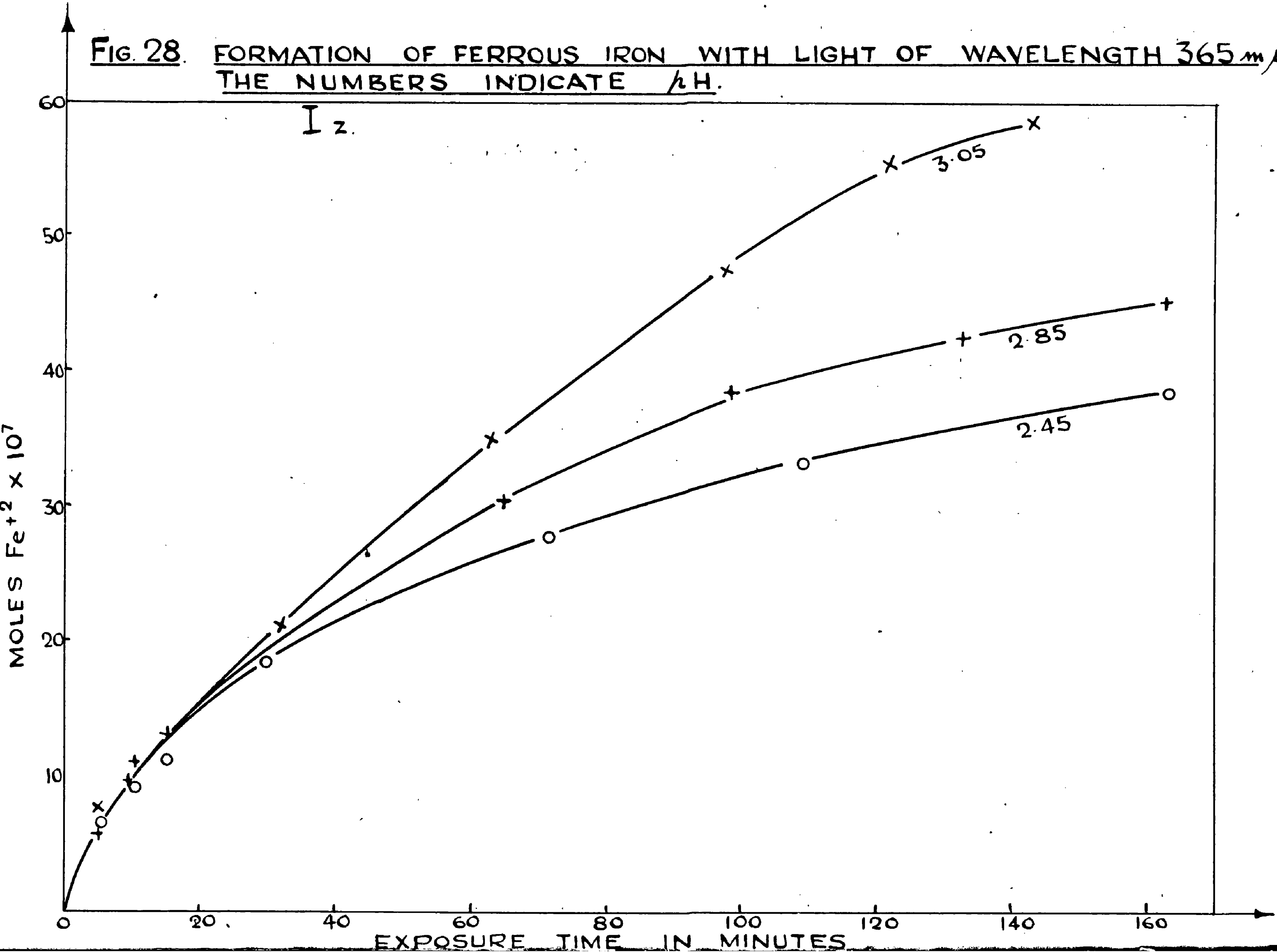
B. Effect of p_H on photo-reduction.

Fig. 28 shows the rate of ferrous ion formation when solutions of 0.0013 $\bar{M}$ ferric chloride of various p_H's (3.05, 2.85, 2.45) were exposed to light of wavelength 365 mμ at 20°C. in large cell.

The accuracy of the analytical method is not sufficient to assert that the initial rates are slightly different as might appear, and they are consequently drawn co-incident. However, as exposure proceeds the curves begin to diverge after 20 minutes to different 'stationary' values, the greater the p_H, the greater is the amount of Fe^{+2} at the 'stationary' level.

Hydrolysis of the iron to ferric hydroxide began early in the exposure of the solution at p_H 3.05 as found by conduction measurements and visual observation of the brown colour after exposure. The solutions of lower p_H showed no change of conductivity on exposure and remained colourless.

FIG. 28. FORMATION OF FERROUS IRON WITH LIGHT OF WAVELENGTH 365 m
THE NUMBERS INDICATE pH.



The shape of reduction-time curve is the same as was found in experiments with polychromatic light (Part I of this thesis), but the amount of ferrous ion formed is of a different magnitude. A comparison between the two systems is best made by comparing the stationary Fe^{+3}/Fe^{+2} ratio in each (termed R).

(1) Polychromatic light Experiments.

The light source was the unfiltered Hanovia U.V.S. 500 lamp. At p_H 2.85,

$$[Fe^{+2}]_{stationary} = 58.5 \times 10^{-6} \text{ moles (Fig. 2 }\underset{\text{Curve 5}}{)}$$

Volume of solution = 300 ml.

$$\text{i.e. } [Fe^{+2}]_s = 58.5 \times \frac{1000}{300} \times 10^{-6} = 1.95 \times 10^{-4}\bar{M}$$

$$\therefore \quad [Fe^{+3}]_s = (13-1.95) \times 10^{-4}\bar{M} = 11.05 \times 10^{-4}\bar{M}$$

$$\therefore \quad R = \frac{11.05}{1.95} = \underline{5.66}.$$

(2) Wavelength 365 mµ.

Light source. 250 W. MED. LAMP

The solutions had not reached a stationary state with the exposure given (Fig.28) but a reasonably accurate estimate can be made.

At p_H 2.85,

$[Fe^{+2}]_s = 4 \times 10^{-6}$ moles.

Volume = 136 ml.

$\therefore \quad [Fe^{+2}]_s = 2.94 \times 10^{-5}\bar{M}$

$\therefore \quad [Fe^{+3}]_s = (13-0.294) = 12.71 \times 10^{-4}\bar{M}$

$\therefore \quad R = \frac{12.71}{0.294} = \underline{43.2}.$

This higher value of R with monochromatic light could be due to the smaller light intensity and or the exclusion of other photo-active wavelengths. The effect of light intensity on the stationary ferrous value was therefore investigated.

C. The Effect of Light Intensity.

The solution studied was of p_H 2.85, T = 20°C. and exposed to λ 365 mμ in the large cell (optical depth 7 cm.).

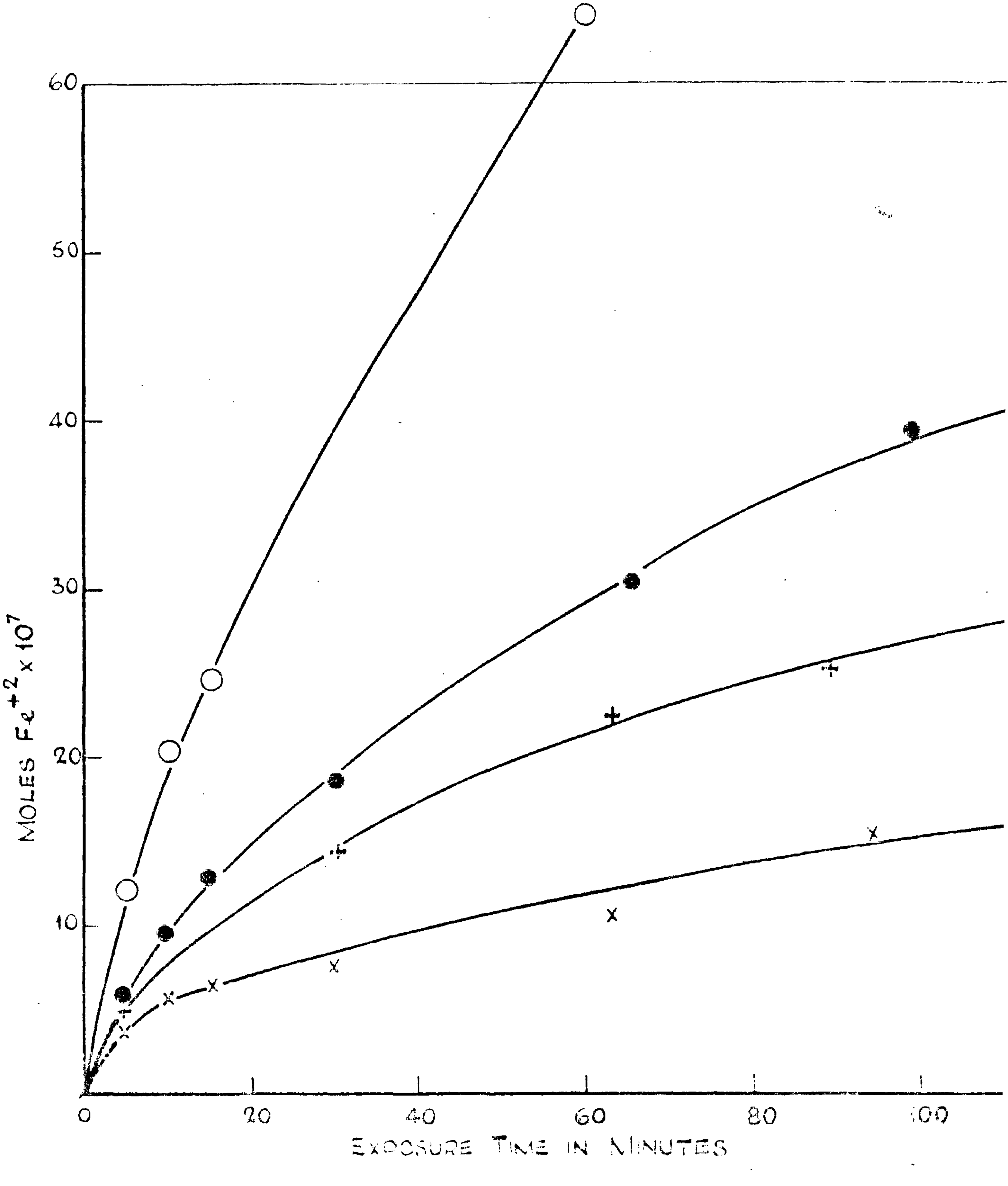
A decrease in light intensity not only results in a lower initial rate of reduction, as expected, but also affects the stationary state as shown in Fig. 29.

The relationship between Intensity and $(\frac{d\,Fe^{+2}}{dt})_{initial}$

FIG. 29. EFFECT OF LIGHT INTENSITY ON THE REDUCTION-TIME CURVE

THE NUMBERS INDICATE ($N.h.\nu \times 10^6$) PER MINUTE

O, FULL BEAM.



was experimentally difficult to decide. This is due to two things -

(a) the approach of the curve to the origin is curving rapidly,

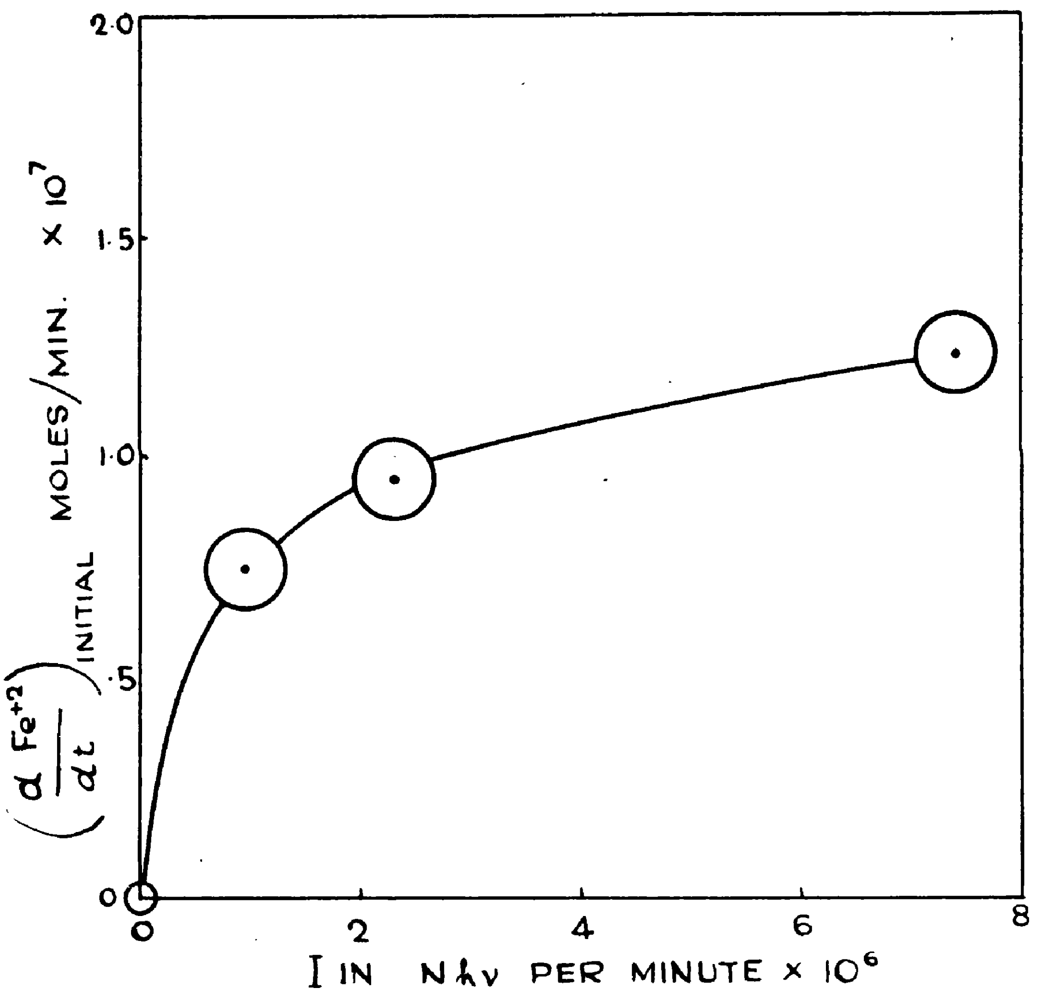
(b) because of (a) all the greater accuracy in the knowledge of ferrous concentration with small exposures is essential, this in solutions of ferrous ion of the order $10^{-6}\overline{M}$.

Absorption measurements (described previously Fig.16 indicate that in the solution used here absorption of λ 365 mμ is complete in a thickness of $\sim$ 2 cm. of solution. Therefore in the present system the absorption fraction $k_{\varepsilon} = 1.0$.

The plot $\left(\frac{d\,Fe^{+2}}{dt}\right)_{initial}$ against I is shown in Fig. 30. The mathematical correlation is not clear. In view of the low accuracy it might well be that $\left(\frac{d\,Fe^{+2}}{dt}\right)$ is proportional to the square root of the intensity, for example.

However, there is little error involved in a correlation of I with 'stationary' Fe^{+2} values. Although the stationary values were not reached during the exposure time, $\left(\frac{d\,Fe^{+2}}{dt}\right)$ decreases sufficiently with each

FIG. 30.



2·0
1·5
1·0
·5
0
0
2
4
6
8
$\left(\frac{d\,Fe^{+2}}{dt}\right)_{INITIAL}$ MOLES/MIN. × 10^7
I IN $Nh\nu$ PER MINUTE × 10^6

light intensity to allow an arbitrary assumption of stationary conditions after, say, 160 minutes which if not 'absolutely' correct should be 'relatively' so. A plot of this stationary $[Fe^{+2}]$ against $\sqrt{I}$ is found to be a linear function, passing through the origin (Fig. 31).

An increase in light intensity was achieved using the full beam of the lamp. The effect on the ferrous ion formation is shown in Fig. 29 - increased initial rate and proceeding to a much higher stationary value.

D. The Quantum Yield.

In experiments using the large quartz cell the estimated initial values of $\frac{d\,Fe^{+2}}{dt}$ were rather inaccurate (~~see inset Fig. 30~~).

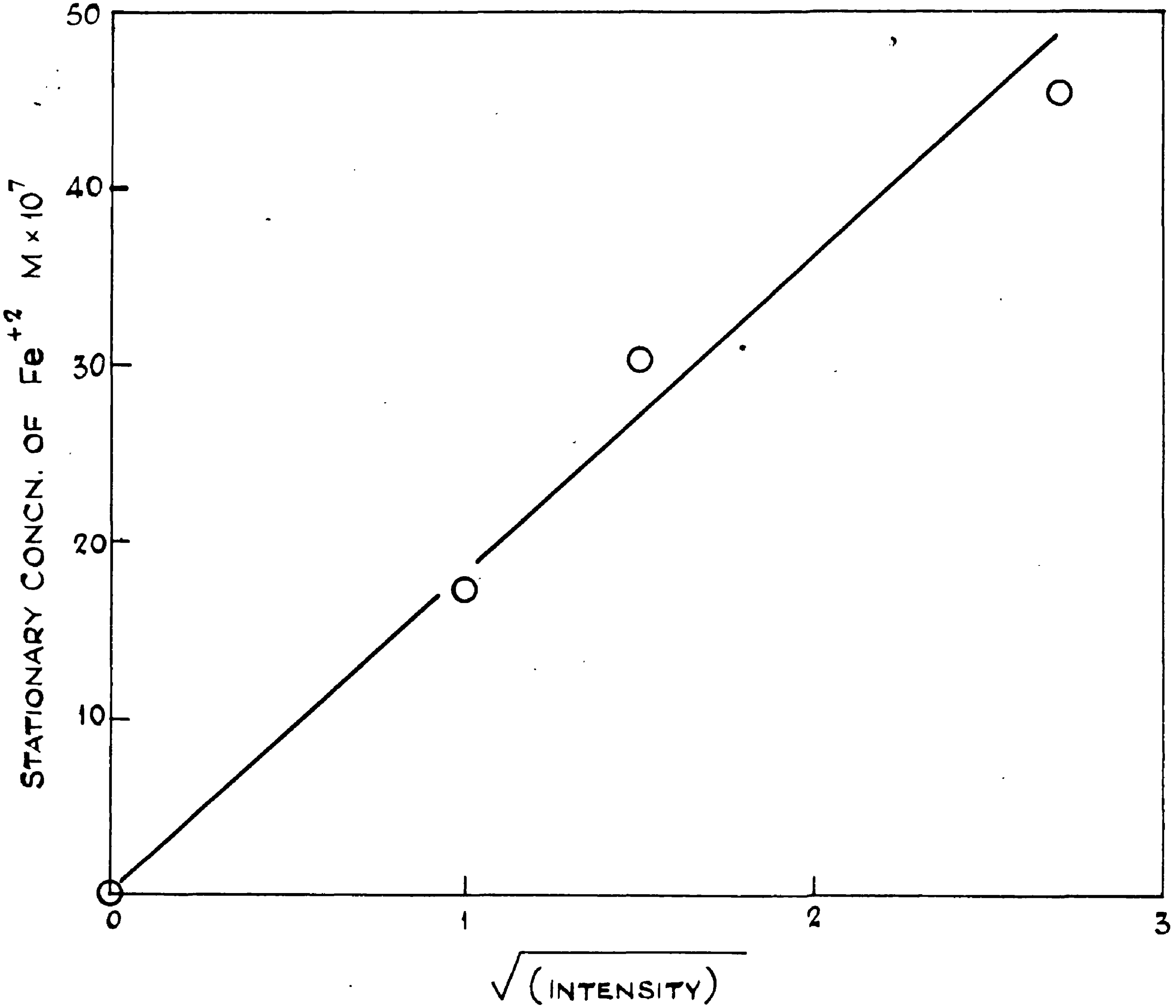
For a quantum yield calculation values of intensity and initial rates of ferrous ion formation were taken from Fig. 30 .

$$\text{max} = \frac{d\,Fe^{+2}/dt}{k_{\varepsilon} I} \qquad k_{\varepsilon} = 1.0$$

$$= \frac{1.2 \times 10^{-7}}{6 \times 10^{-6}} \qquad \frac{d\,Fe^{+2}}{dt} = 1.2 \times 10^{-7} \text{ moles/min.}$$

$$= \underline{0.020}. \qquad I = 6 \times 10^{-6} \text{ NhV/min.}$$

FIG. 31.


50
40
30
20
10
0
1
2
3
STATIONARY CONCN. OF Fe^{+2} $M \times 10^7$
$\sqrt{(\text{INTENSITY})}$

A more accurate result was found using the smaller cell (optical depth 2 cm.) as discussed on part because this method permits of a more accurate Fe^{+2} analysis. The plot of $[Fe^{+2}] \propto$ exposure time is shown in Fig. 32.

$$\gamma_{\text{max.}} = \frac{d\,Fe^{+2}/dt}{k_{\varepsilon}\, I} \qquad k_{\varepsilon} = 1.0$$

$$= \frac{1.5 \times 10^{-7}}{5.8 \times 10^{-6}} \qquad \frac{d\,Fe^{+2}}{dt} = 1.5 \times 10^{-7}\ \frac{\text{moles}}{\text{min.}}$$

$$= 0.026. \qquad I = 5.8 \times 10^{-6}\ Nh\nu/\text{min}$$

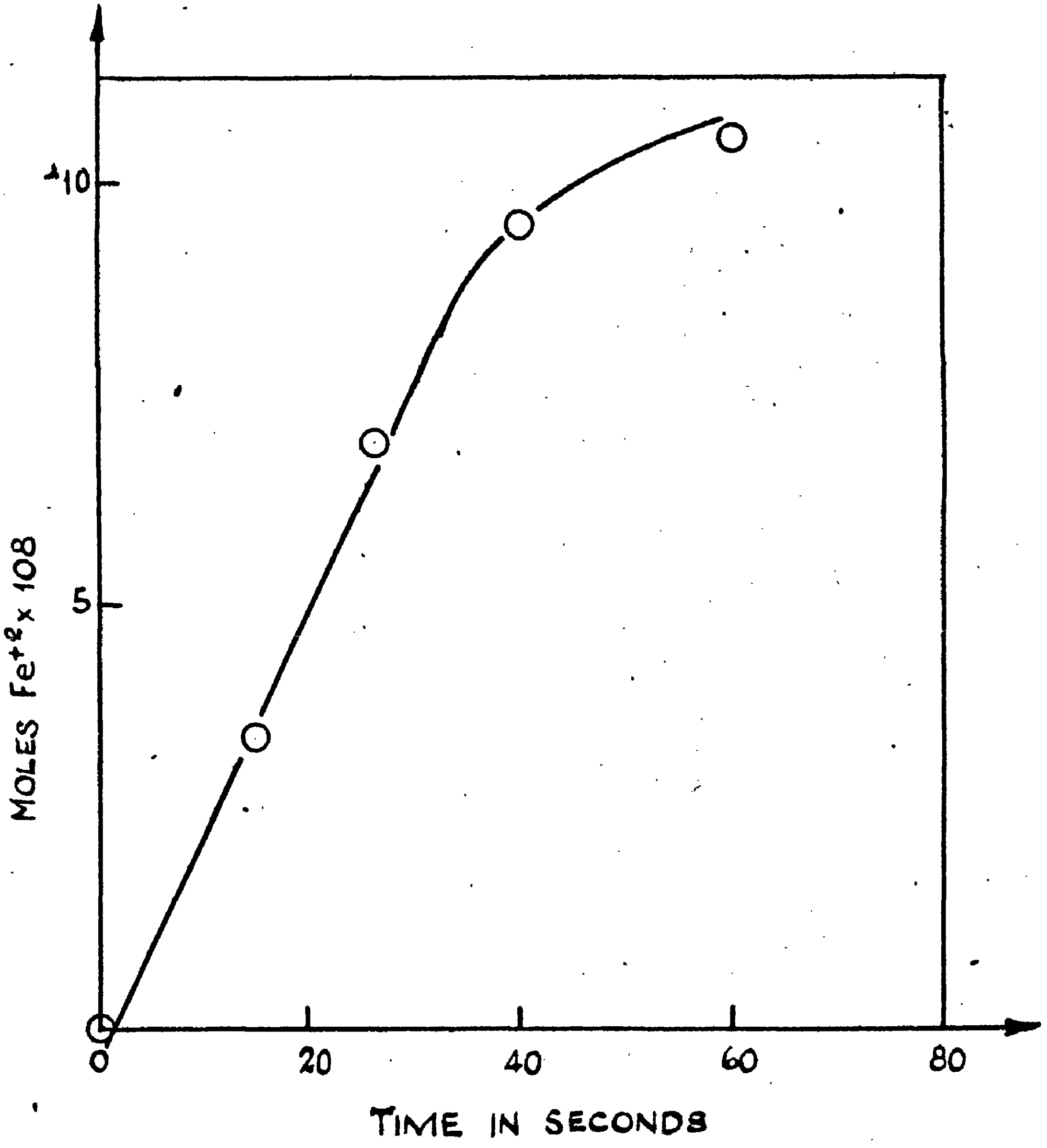
Thus the two values are in good agreement.

E. The Role of Ferric Hydroxide.

It was noted while studying the effect of p_H on photo-reduction that at the high p_H of 3.05 secondary hydrolysis took place during the exposure, detected by the increase in conductivity of the solution (due to liberation of H^+).

An increase in photo-activity with the appearance of hydrolysis having been found in the work with polychromatic light (Part I) it was decided to attempt to detect this phenomenon using monochromatic light of

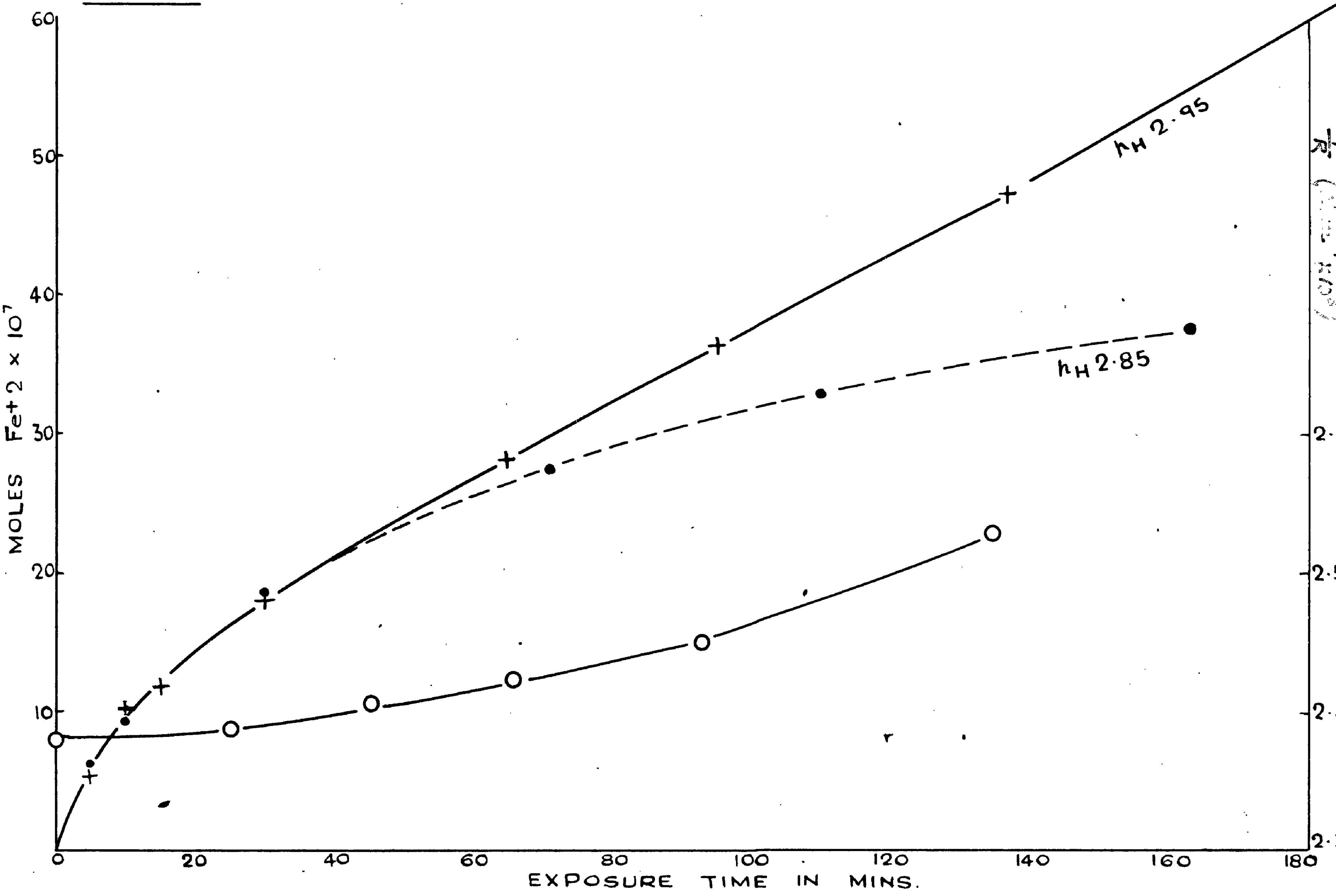
FIG 32. LIGHT INTENSITY = 5.8×10^{-6} N h J PER MINUTE



365 mμ. The hydrolysis had to be retarded until well on in the exposure, when a stationary state was setting in, so that an increase in photo-activity might easily be recognised. This was achieved with a solution of p_H 2.95 and the expected increase in photo-reduction was readily observed (Fig. 33). For purposes of comparison the photo-reduction of a solution of p_H 2.85 at same light intensity is shown as a dotted curve on the same figure. The reduction follows the same path with both solutions until the one at the slightly higher p_H begins to hydrolyse (as shown by the conductivity) when it then shows no trend to an equilibrium level as does the other one, indeed the curvature changes from convex up to linear or even concave up. It was also found that initiation of hydrolysis is brought about by light of this wave-length (see also Part 5).

The brown colour of hydrolysis is attributed to colloidal $Fe(OH)_3$ absorbing light in the region 425 mμ. An experiment was designed to show if the colloidal $Fe(OH)_3$ was photo-active in this region. Using the filter '0.5 cm. saturated sodium nitrite' all light

FIG. 33

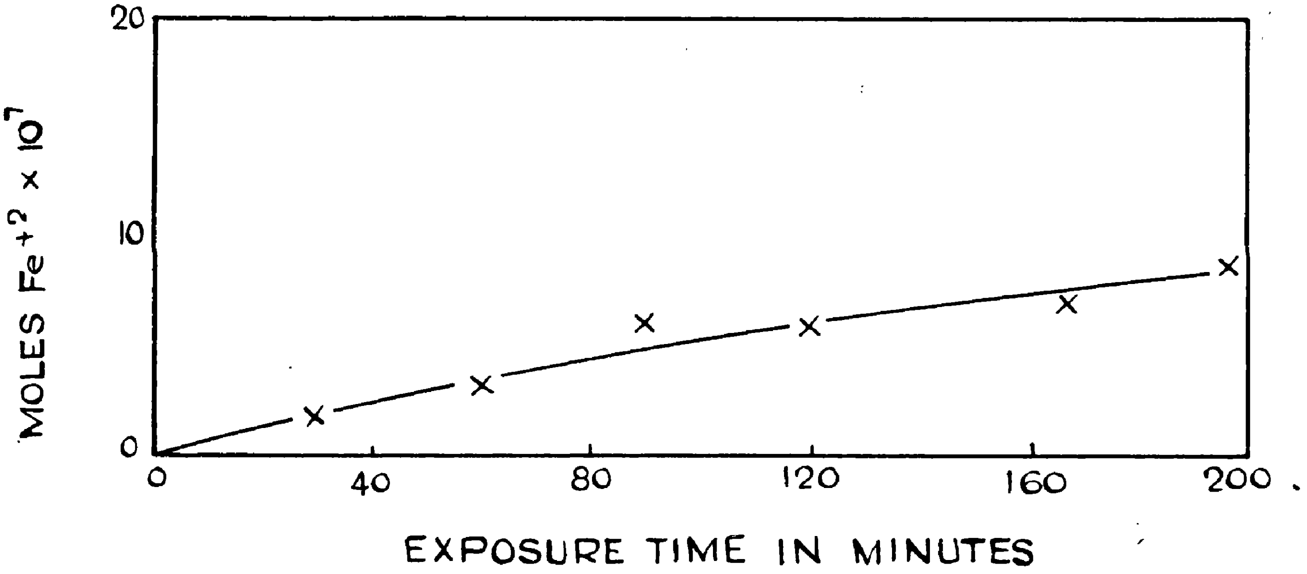


60
50
40
30
20
10
0
20
40
60
80
100
120
140
160
180
MOLES $Fe^{+2} \times 10^7$
EXPOSURE TIME IN MINS.
h_H 2·95
h_H 2·85

of $\lambda < 420$ mµ was cut off and the iron solution of p_H 3.0 was exposed to these larger wavelengths. Fig. 34 shows a very small photo-reduction takes place. The solution hydrolyses during exposure.

FIG 34

$\lambda > 420\ m\mu$



Discussion.

Actinometry.

Actinometry by Parker's[1] method was found to be a very simple procedure, and because of this, together with the high analytical accuracy, it should soon be preferred to the uranyl oxalate actinometer by a growing number of photochemists.

The Effect of p_H on photo-reduction.

The results indicate that there is little difference in the initial rates of photo-reduction as the p_H is raised from 2.45 to 3.05. However the 'stationary' values are seen to rise with increase of p_H, presumably due to the competing reactions

$$Fe^{+2} + OH \rightarrow Fe^{+3} + OH^- \;\ldots\ldots\ldots\ldots(1)$$

$$Fe^{+3}OH^- + OH \rightarrow Fe^{+2} + H_2O_2 \ldots\ldots\ldots\ldots(2)$$

$$Fe_2(OH)_2^{+4} + OH \rightarrow Fe^{+3}OH^- + Fe^{+2} + H_2O_2 \ldots(3)$$

The greater the concentration of $Fe^{+3}OH^-$ or 'dimer', the higher should be the yield of Fe^{+2}. The increase in the concentration of these species when the p_H in-

---

[1] Parker, Proc.Royal Soc., 1953, A 220, 104.

increased from 2.08 to 3.08 is shown in Table 5 (page 86).

The slopes of the reduction time curves ~~is~~ are similar to ~~that~~ those for polychromatic light.

The Effect of Light Intensity.

Fig. 30 shows that $(\frac{d\,Fe^{+2}}{dt})$ is <u>perhaps</u> proportional to $\sqrt{I}$. The maximum yield of ferrous ion, i.e. $[Fe^{+2}]_{stationary}$ is also proportional to $\sqrt{I}$. This is experimental evidence for Uri's suggestion that because of the two competing reactions, (1) and (2) above very high light intensities would be required to obtain measurable quantum yields.

Because of the square root function an increase of I by a factor of 100 would only change $[Fe^{+2}]_s$ by a factor of 10. It is obvious then that the reason for the large difference in magnitude of $[Fe^{+2}]_s$ with the Hanovia lamp, U.V.S. 500 (unfiltered) and the monochromatic light from the 250 W.ME.D. lamp is most likely to be due to the large difference in light intensity. With the former lamp the flasks approach to within 4 cm. of the lamp, while with the latter light source the solution is at a fixed distance of $\sim$18 cm. from the lamp. Intensity is inversely proportional to the square of the distance.

The Quantum Yield.

The accurate value of maximum quantum yield (γ) found in these experiments, i.e. $\gamma_{Fe^{+2}} = 0.026$.

$$\gamma = \frac{d\,Fe^{+2}/dt}{k_{\varepsilon}\, I}$$

~~and since $\frac{d\,Fe^{+2}}{dt} \propto I$ then γ is independent of light intensity.~~

Assuming that photo-oxidation of water still takes place at low light intensities, and that the reduction is not due to impurities, then

$$\gamma_{O_2} = \frac{1}{4} \times \gamma_{Fe^{+2}} \equiv 6.5 \times 10^{-3}$$

The quantum yield, measured by Dain and Kachan[2] for the photo-oxidation of water by the species $Fe(H_2O)_6^{+3}$ is of the order 10^{-3}.

Weiss[3] stated that with irradiated ferric perchlorate solutions, containing the species $Fe^{+3}OH^-$, it could only be concluded that $\gamma_{O_2} < 10^{-2}$ as their apparatus was not sensitive enough below this value.

---

[2] Dain and Kachan, Doklady Akad.Nauk.S.S.S.R.,1948,61,471

[3] Weiss, Symposium No. 8. CO_2 function and Photosynthesis, Soc. for Exp. biology, Sheffield, 1950.

Therefore γ_{O_2} found in the present work would seem to be of the correct order of magnitude.

PART IV.

THE HETEROGENITY OF THE SYSTEM

Introduction.

Experimental results described in Part's I and III of this thesis show quite beyond doubt that colloidal ferric hydroxide plays a major part in the photo-reduction. There are a number of possible explanations as to the mechanism of this increased photo-activity shown on hydrolysis, and these are discussed after the experiments, described below.

The formation of hydrogen peroxide is suggested as an intermediate in this 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 hydrolysis on peroxide decomposition.

A heterogeneous effect in the photo-oxidation of water, when the vessels were packed with silica, was reported by Dain and Kachan[1]. Increased oxygen evolution was observed and it is suggested that the surface catalyses the recombination of OH radicals.

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

A similar effect might be expected with iron solutions and an investigation of this aspect was initiated.

---

[1] Dain and Kachan, Doklady.Akad.Nauk., 1949, 67, 85.

Experimental and Results.

A. The Catalytic Decomposition of H_2O_2 by Ferric Iron.

Materials. The hydrogen peroxide was Laporte's 88% A.R. material (unstabilised). A stock solution was prepared from this with distilled water and dilutions made from the stock to the required concentrations.

The ferric chloride solutions were prepared as before.

Experimental Method. It was decided to follow the rate of decomposition of hydrogen peroxide with $1.3 \times 10^{-3} \bar{M}$ Fe^{+3} under different solution conditions of the iron.

(1) No hydrolysis.

(2) Hydrolysis beginning during the reaction.

(3) Hydrolysis well under way before reaction,

in order that the effect of colloidal ferric hydroxide could be observed.

t/ The iron solutions were prepared and thermostated. Then 5 ml. of stock H_2O_2 solution was pipetted into 500 ml. of iron solution with vigorous stirring, to give a 1.25 $\bar{N}/40$ H_2O_2 solution and a sample immediately withdrawn for peroxide analysis with permanganate. The sample was delivered into a conical flask containing N/5 H_2SO_4 which stopped any further reaction before titration. The reaction was thus followed by titration of samples withdrawn at noted time intervals, and graphs shown are plots of Mls.$KMnO_4$ v. reaction time.

The hydrolysis was detected by the formation of a reddish-brown colour measured on a Hilger 'Spekker' as described before in Part 1.

Fig. 35 shows the decomposition of hydrogen peroxide under solution conditions (1) and (2) above. The full line is the rate of peroxide decomposition and the dotted lines indicate the position of the hydrolysis as shown by absorption measurements. The hydrolysis was delayed until reaction time by ageing solution at 20°C. It is seen that the appearance of colloidal ferric hydroxide has no effect on the peroxide decomposition.

A comparison is made in Fig. 36 of the decomposition of 3.15 $\bar{M}/40$ hydrogen peroxide using,

(a) solution with no hydrolysis,

(b) solution aged 4 hrs. at 20°C. before hydrogen peroxide added, i.e. about 30% hydrolysis before reaction.

The colloidal ferric hydroxide seems to be a less efficient catalyst than a solution of ferric ions.

FIG. 35

THE DECOMPOSITION OF H_2O_2 BY FERRIC IRON, SHOWING THE ABSENCE OF AN EFFECT ON THE APPEARANCE OF COLLOIDAL FERRIC HYDROXIDE.

—— CONCN. OF H_2O_2.
- - - - EXTINCTION OF Fe/H_2O_2 SOLN. (301 FILTER 4 cm CELL.)

X Fe SOLN., pH. 2·95, ZERO AGE, PLUS H_2O_2

O Fe SOLN.; pH. 2·95 AGED 45 MINS. BEFORE MIXING WITH H_2O_2 (IN ORDER THAT HYDROLYSIS TAKES PURE DURING H_2O_2 DECOMP.)

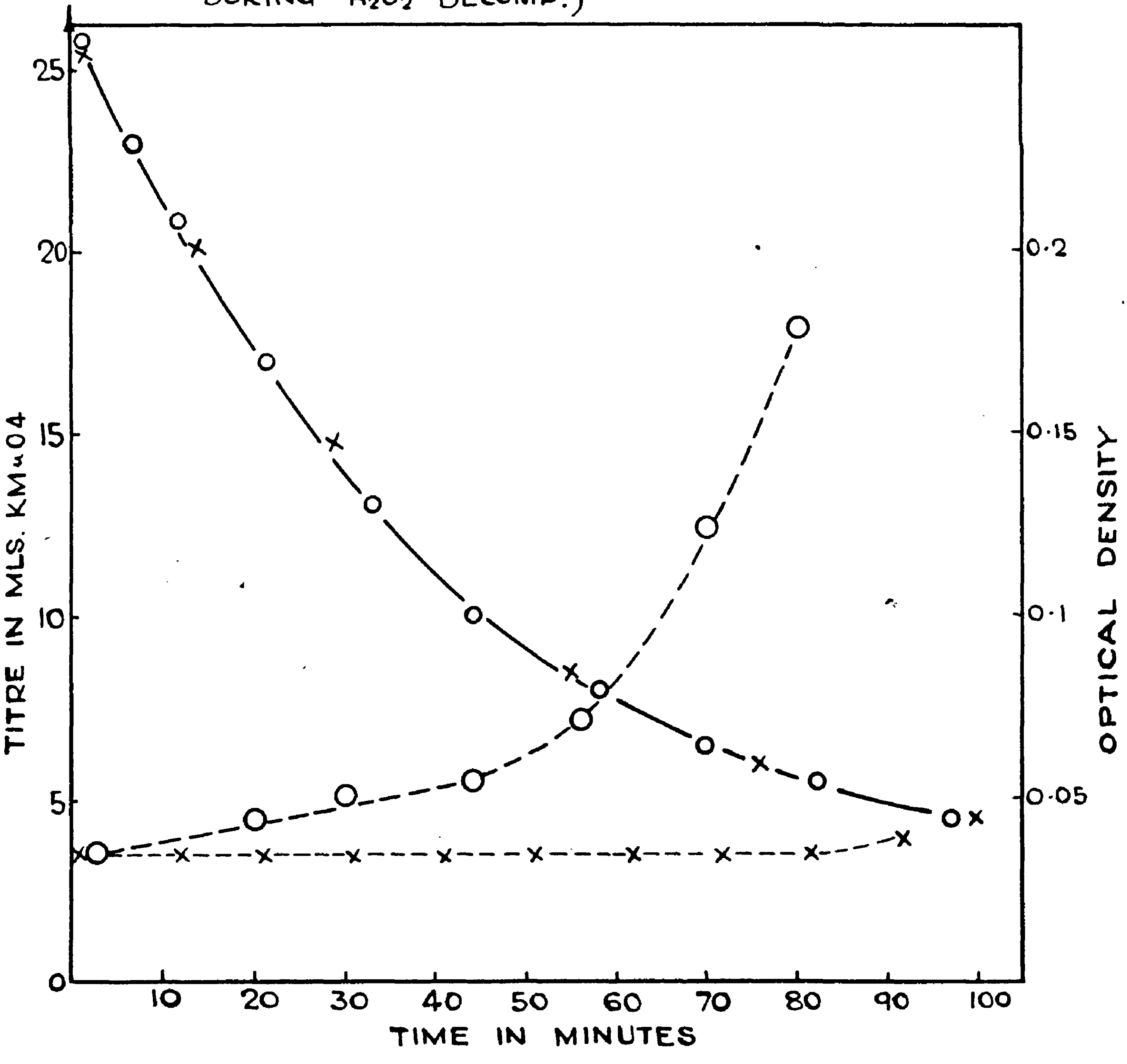
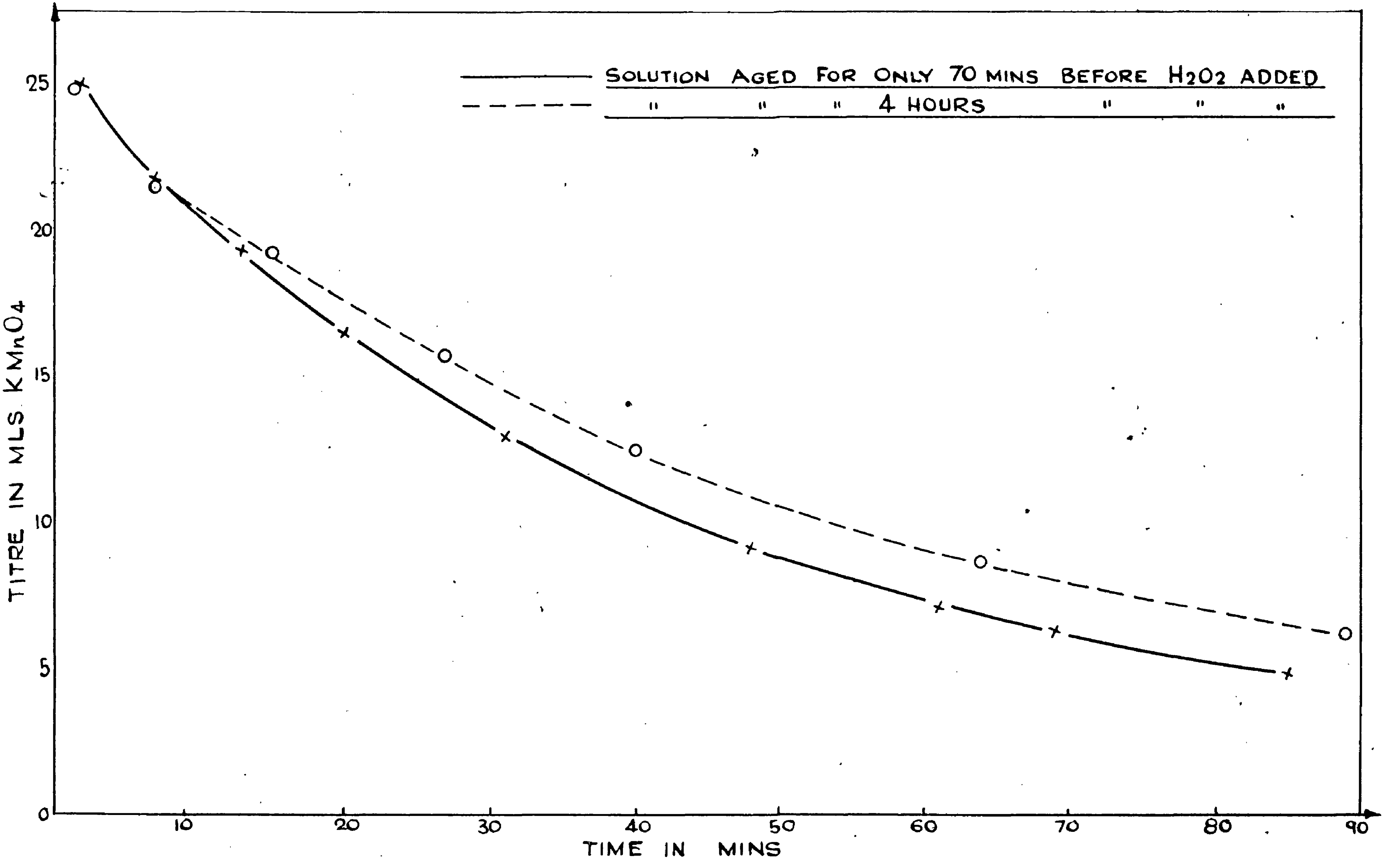


FIG. 36 THE DECOMPOSITION OF H_2O_2 BY Fe^{+++} $Fe^{+++}{}_2$ $1{\cdot}3 \times 10^{-3}\bar{M}$,
PN + 3·05 $H_2O_2{}_2$ 3·15 $\bar{N}/40$



B. The Effect of Finely Powdered Silica on Photo--Reduction.

Materials. The silica used was the iron-free silica gel used for the preparation of phosphors as described in Part II. The purified gel was crushed to a fine powder in an agate mortar.

Experimental Method and Results.

In order to minimise a possible objection that the gel may contain oxidisable organic impurities a portion of it was stirred with fresh portions of 1 $\bar{M}$ H_2O_2 daily for three weeks. About 20% decomposition of the peroxide took place in 6-8 hours. The gel was then washed daily with distilled water for a further six weeks to remove the peroxide.

The solution investigated was $1.3 \times 10^{-3}\bar{M}$ ferric chloride of p_H 2.45, this acidity being used to prevent hydrolysis during irradiation. Hydrolysis would complicate interpretation of any effects found with the silica as two surfaces would be present, one due to colloidal ferric hydroxide and one due to the silica.

The reaction conditions were 5 g. silica 150 ml. of iron solution.

When the system was stirred in the dark a decrease in ferric iron concentration was found by analysis with titanous chloride solution. Moreover no Fe^{+2} was detected (with o-phenanthroline) so the iron must be adsorbed by the silica. Such adsorption is well known. Here ~~it~~ the adsorption varied between 15 and 25%.

The solution was stirred and irradiated by the Hanovia S.500 lamp for 20 minutes at a distance of 8 cm. The percentage photo-reduction of the iron was measured in two ways.

(a) The solution was stirred in the dark for 30 minutes before irradiation and a sample withdrawn for iron analysis in order to find the percentage adsorption. The solution was then irradiated after which the Fe^{+3} was again estimated and the percentage photo-reduction calculated. This method assumes that 20 minutes is sufficient for maximum adsorption and that this adsorption is unaltered by the irradiation.

(b) After irradiation the solution was analysed for Fe^{+2} by o-phenanthroline and the percentage reduction calculated. This assumed that no

~~that no~~ Fe^{+2} was adsorbed. If Fe^{+2} was adsorbed then the true photo-reduction will be higher, i.e. this calculated photo-reduction is a minimum value.

The results are summarised in Table 10.

Initial Fe^{+3}	% Adsorption	Total % decrease in Fe^{+3} after irradiation	% Photo-reduction	$\bar{M}$ of Fe^{+2} Prod.	% Photo-reduction	'Blank' % Red.
1.3×10^{-3}	16.5	34.7	18.2	2.47×10^{-4}	19.0	6.1
1.3×10^{-3}	23.2	40.0	16.8	2.18×10^{-4}	16.8	6.1
1.3×10^{-3}	18.1	35.1	17.0	2.52×10^{-4}	19.4	6.1

The results show a good reproducibility and the assumptions above with regard to the calculation of photo-reduction seem justified since the two methods agree so closely.

The 'Blank' reduction is of course the same experiment but without added silica.

The increased yield of Fe^{+2} indicates a heterogeneous reaction on the surface of the silica. This result is analogous to that in the ceric ion silica U.V. system in which an increased cerous and oxygen yield was observed by Dain and Kachan.

It is considered that an increased oxygen yield will be found in the present system too. A start was made to decide this point using the oxygen detection apparatus described in Part II.

It was soon found however, that the technique hitherto used for preliminary degassing of the system was inadequate presumably due to the great slowness with which, in these conditions, the adsorbed gas in the silica gel powder is given up.

Because of lack of time the experiments had to be discontinued at this stage.

Discussion.

There are two main possibilities for the role of colloidal ferric hydroxide in this photo-oxidation of water by ferric ion.

(1) The species is photo-active.

(2) The surface catalyses a dark reaction(s) leading to a higher oxygen yield.

(1) The photo-activity of the species must be doubtful because the increase in $\frac{dFe^{+2}}{dt}$ happens on the appearance of hydrolysis, i.e. a large, fresh surface. If exposure is delayed until hydrolysis is well under way, i.e. the surface is 'aged', the photo-activity falls (Fig. 9). Therefore there is a fall in photo-activity when the reaction

$$\text{Ferric Ion} \rightarrow Fe(OH)_3 \text{ (colloidal)}$$

is far over to the right.

On hydrolysis there is a large increase in absorption above 400 mμ (solution turns reddish-brown). A solution hydrolysed during exposure to an intense beam of wavelength 420 mμ, was found to have a very small photo-activity (Fig. 34).

(2) Considering the contribution of $Fe(OH)_3$ to be a catalytic dark reaction the importance of a 'fresh' and large surface area, found within the first hour or two of hydrolysis at the high p_H's is evident.

As hydrolysis proceeds, and the particles grow, the surface area per unit mass rapidly falls as also the concentration of the photo-active ion-pairs.

Powdered silica was found to increase the Fe^{+2} yield in the present system. In the analagous photo-oxidation of water by ceric ion the heterogeneous reactions found on the silica surface is attributed to recombination of OH radicals on the surface.

Therefore although hydration might radically change the surface properties a possible surface reaction of colloidal ferric hydroxide is

$$OH + OH + Fe(OH)_3 \longrightarrow H_2O_2 + Fe(OH)_3$$

which would of course compete with the back reaction

e/

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

and therefore lead to a higher Fe^{+2} and oxygen yield.

It is also possible that the surface of the colloidal ferric oxide catalyses an electron transfer reaction leading to higher oxygen yield.

Waind[2] studied the heterogeneous catalysis of some inorganic reactions which have been formulated as electron transfer, e.g. the Tl(I) - Tl(II) exchange is catalysed by platinum black, and the reaction

$$Hg(II) + Fe(II) \rightarrow Hg(I) + Fe(III)$$

is catalysed by an iron surface.

It is suggested that in all such cases the catalyst is acting as a conductor.

---

[2] Waind (Mrs.), *Chem. and Ind.*, 1955, 1388.

PART V.

THE EFFECT OF LIGHT ON HYDROLYSIS.

Introduction.

It has long been recognised that ferric chloride when dissolved in water is not only subject to the usual instantaneous hydrolysis characteristic of the salt of a strong acid and a weak base, but also, except in concentrated solution, undergoes a further relatively slow hydrolysis, which, depending on the circumstances, may require an interval varying from a few moments to a month or more for its completion. This slow hydrolysis is attended not only by a progressive increase in the conductivity and acidity of the solution, but also by the formation of a reddish-brown colloidal solution from which ferric hydroxide may ultimately precipitate.

This surprisingly slow hydrolysis of a highly ionised inorganic salt, accompanied by so striking a colour change has been the object of a great number of investigations since the end of last century. The earlier ones are reviewed in three excellent digests[1,2,3].

---

[1] Gmelin, 'Handbuch der Anorganischen Chemie', 8th Edition, Iron. Part B., Verlag Chemie, Berlin, 1929, pp. 272-278.

[2] Abegg, 'Handbuch der Anorganischen Chemie', Vol. IV, Iron and Its Compounds, Part B. S. Hirzel, Leipzig, 1930, pp. 187-192.

[3] Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Vol. XIX, Longmans, Green and Co., N.Y., 1935, pp. 59-65.

There was however a wide divergence in the explanations put forward by these early investigators.

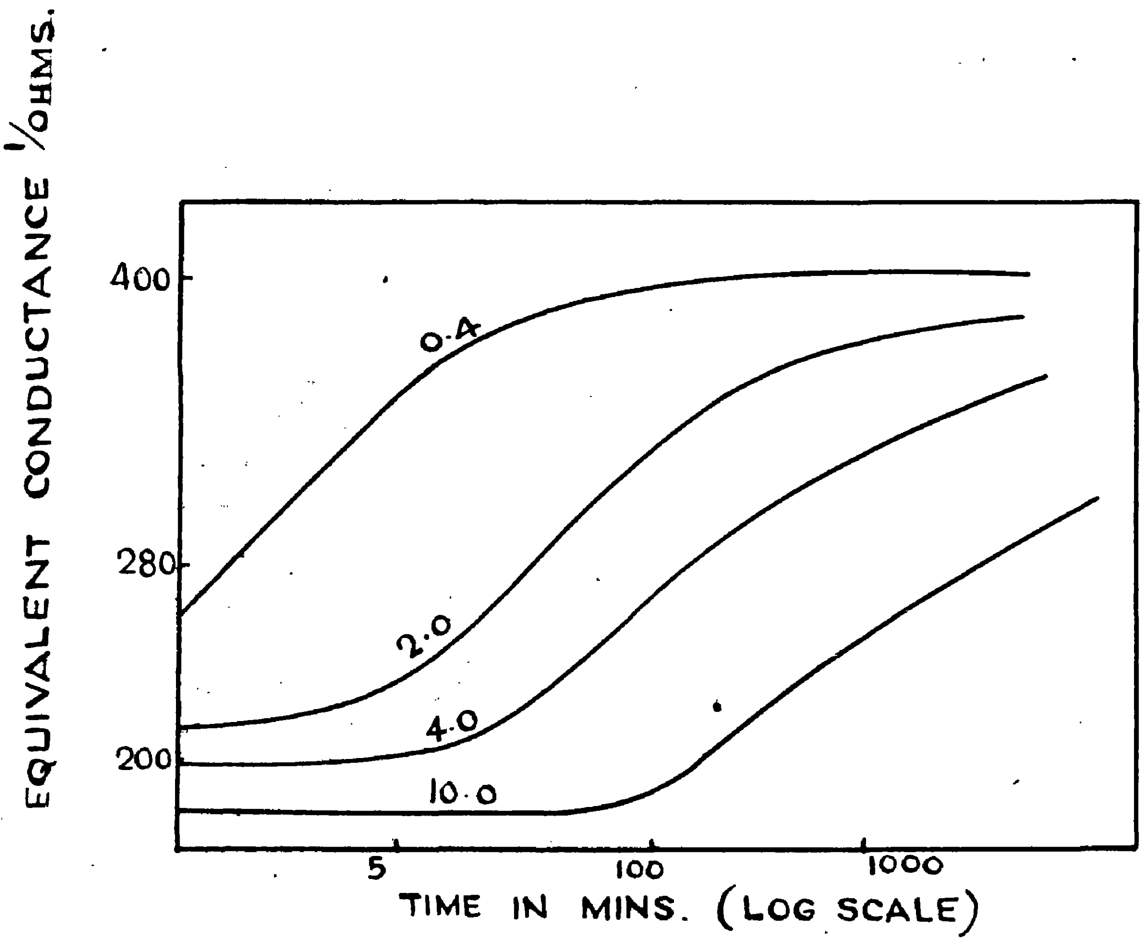
It was Lamb and Jacques[4] who first attempted a quantitative correlation of their experimental data with a proposed mechanism. They investigated the phenomenon by means of conductivity, colorimetric and electrometric measurements. The previously observed marked increase in the speed of the hydrolysis with increasing dilution and temperature, and the induction period in the most concentrated solutions were confirmed. The previously observed pronounced decelerating effect of acids such as hydrochloric and nitric was also confirmed. The general slope of the hydrolysis rate curves is shown in Fig. 37 where the effect of dilution is taken from Lamb and Jacques paper. The induction period is apparent at concentration 0.0013 $\overline{M}$ and higher. Here the progress of the hydrolysis is at first barely perceptible; gradually, however, it increases and then finally decreases as hydrolysis becomes nearly complete.

The explanation advanced for the phenomenon was that as soon as the ferric salt dissolves a rapid

---

[4] Lamb and Jacques, J.A.C.S., 1938, 1, 967, 1215.

FIG. 37. (FROM LAMB & JACQUES) THE NUMBERS INDICATE CONCENTRATION OF THE IRON SALT IN MILLIEQUIVALENTS NORMAL.



reversible hydrolysis ensues giving rise to a variety of hydrolysis products but in particular to a dilute, nevertheless supersaturated, solution of ferric hydroxide.

$$Fe^{+++} \overset{H_2O}{\rightleftharpoons} \underset{\substack{+\\H^{+}}}{Fe(OH)^{++}} \overset{H_2O}{\rightleftharpoons} \underset{\substack{+\\H^{+}}}{Fe(OH)_2{}^{+}} \overset{H_2O}{\rightleftharpoons} \underset{\substack{\text{in soln.}\\+\\H^{+}}}{Fe(OH)_3} \rightleftharpoons \underset{\text{colloidal}}{Fe(OH)_3}$$

The coagulation of this substance to form colloidal ferric hydroxide is the controlling, relatively slow step, in this reaction. The rate of hydrolysis is proportional to the degree of supersaturation of the undissociated ferric hydroxide. The experimental results can be explained on this basis.

This hypothesis was later supported by Bovalini and Niccolini[5] who studied the hydrolysis of the sulphate nephelometrically with a Pulfrich photometer.

Recent work on ferric iron hydrolysis has been directed to the measurement of the hydrolytic equilibrium constants. This is reviewed by Hedström[6] who, from his own investigation on the hydrolysis by electrometric measurements, postulated the existence of a

---

[5] Bovarini and Niccogini, *Gazz.Chem.Ital.*, 1948, *78*,242.

[6] Hedström, *Arkiv.Fur Kemi.*, 1953, p. 1-16.

polynuclear complex of the form $Fe_2(OH)_2{}^{4+}$.

Further evidence of polynuclear species was found by Malay and Selwood[7,8] in a magnetic and spectrophotometric study of ferric perchlorate solutions.

Early this century in a spectrophotometric investigation Moore[9] found that light had no effect on initiation of the hydrolysis of ferric iron.

Foussereau[10] had previously reported that some of the hydrosol of ferric hydroxide might be coagulated by the action of light. This was amplified by Schild[11] and by Roeser[12] who found coagulation only occurs when some ferrous chloride is present.

Bhatnager[13] and co-workers found that exposure to X-rays favours the hydrolysis.

An increase in the rate of coagulation of Fe_2O_3 solutions by exposure to light was detected by Zocher and Heller[14] and was further investigated by Heller[15]

---

[7]

[8] Malay and Selwood, J.A.C.S., 1955, 77, 2693.

[9] Moore, Phys.Rev., 1901, 12, 163.

[10] Foussereau, Ann.Chim.Phys., 1887, 11, 386; 12, 553.

[11] Schild, Berg.Hutt.Ztg., 1888, 47, 251.

[12] Roeser, Jovrn.Pharm.Chim., 1895, 2, 250.

[13] Bhatnager et al., Zeit.Phys., 1929, 56, 692.

[14] Zocher and Heller, Z.Anorg.Allgem.Chem., 1930, 186, 75.

[15] Heller, Compt.Rend., 1934, 199, 723.

It was considered that the increase in coagulation rate was probably due to the critical diminution of the double layer through some photochemical action on the adsorbed electrolyte.

It would then appear, according to these previous studies, that although light is not active in initiation of hydrolysis, a photo-effect in the coagulation of the solution, once formed, is evident.

It was noticed early in the present investigation of the photo-reduction of ferric chloride solutions that with the high dilution and p_H used a reddish-brown colour had formed during the U.V. exposure, whereas another portion of the same solution sitting in diffuse daylight at the same temperature had remained colourless. This colour formation is attributed to the products of secondary hydrolysis, i.e. the formation of colloidal ferric hydroxide[4]. The inference was that the action of light on the iron solution accelerated the initiation of the hydrolysis. This is contrary to the previous findings of Moore[9].

The action of light on the hydrolysis of iron solutions was ther~~n~~efore further investigated with the present system in the hope that the information gained would prove itself of some value with regard to the mechanism of the photo-oxidation of water by ferric iron and also the hydrolytic properties of iron solutions in general.

Experimental.

On dilution all solutions were initially colourless. The hydrolysis was followed by measuring the rate of formation of the reddish-brown colour (attributed to ferric hydroxide) by means of a Hilger 'Spekker' colorimeter equipped with Ilford 601 filters (spectral region 425 mμ) and using 4 cm. cells. When an optical density of 1.0 was reached, about 70% of final value, these cells were replaced by 2 cm. cells, the appropriate cell correction factor thus being used to correlate the measurements.

Solutions whose hydrolysis was followed in the dark, hereafter termed 'dark' hydrolysis, were kept in blackened quickfit conical flasks and thermostated. The 'dark' hydrolysis was followed by pipetting out samples from the blackened conicals. These samples were not returned to the flasks.

The apparatus for the U.V. exposure has been previously described in Part I of this thesis and shown in Fig. 1. In some experiments a 200 watt tungsten lamp was used as a light source, the irradiated solution being thermostated in a glass water bath. The 'light' hydrolysis was measured in conjunction with the photo-reduction by measuring the optical density of each solution as it was removed from the rotating table for iron analysis. In some instances the solution was given a short exposure then its hydrolysis followed in the dark; this is indicated on the relevant graphs with exposure times marked.

It was confirmed that temperature has a very marked influence on the appearance and rate of hydrolysis. This has already been found by previous workers. Great care was therefore taken to ensure that a comparison of the 'light' and 'dark' hydrolysis was being made with solutions at the same temperature (because of the thermostating difficulty associated with the exposure table the temperature control could not be considered better than ± 0.1°C.).

Results.

It is evident that the following conditions and species are present in an irradiated solution though presumably absent in the corresponding 'dark' solution.

(1) A decreased ferric iron concentration due to photo-reduction.

(2) Photo-produced ferrous iron.

(3) The OH radical present assuming a free radical mechanism for photo-reduction.

(4) The formation of H_2O_2, assuming it to be an intermediate in the formation of oxygen which was detected as a reaction product.

In a study of the action of light on hydrolysis all these must therefore be considered and their effects investigated.

(A). Evidence of the Phenomenon.

The effect of light on hydrolysis at 20°C., p_H 3.05, of a $1.3 \times 10^{-3}\bar{M}$ $FeCl_3$ solution is shown in Fig. 4. It is seen that although the exposed solution has an initial boost of the hydrolysis, the 'dark' solution catches up and surpasses it, and there is a large difference between their maximum optical densities (henceforth referred to as E_∞).

This maximum value reached must be a measure of the total ferric iron in solution. The shape of the curves in Fig. 4 is understood on this basis. By some mechanism the action of light initiates the hydrolysis earlier than that of the dark hydrolysis. However as exposure continues the ferric iron concentration steadily diminishes and consequently hydrolysis reaches its end value fairly quickly (i.e. E, the optical density approaches E_∞) and this enables the 'dark' hydrolysis of constant ferric concentration to pass it and proceed to the higher maximum optical density indicative of its higher ferric concentration. Thus

$$[E_\infty]_{dark} - [E_\infty]_{light} = K[Fe^{++}].$$

where $[Fe^{++}]$ = photo-produced ferrous iron and
K = constant

or more simply

$$\frac{[E_\infty]_{dark} - [E_\infty]_{light}}{[E_\infty]_{dark}} = \frac{[Fe^{+++}]_{dark} - [Fe^{+++}]_{light}}{[Fe^{+++}]_{dark}}$$

i.e. % Difference in E_∞ = % Reduction of Ferric Iron.

This conclusion will only be valid if the average particle size of the 'light' and 'dark' $Fe(OH)_3$ solution is approximately the same and small enough to avoid a large Tyndall scattering. This is achieved with the solution 1.3 x $10^{-3}\bar{M}$ Fe^{+++}, p_H 3.05 at 20°C., hydrolysis starting within two hours in both 'light' and 'dark' (Fig. 4) and proceeding quite fast. Portions of this solution were exposed for different times, the reduction measured, and then the solutions thermostated in the dark at 20°C. for two days at which time the optical densities had reached a constant value, i.e. E_∞ achieved. Table 11 lists these values with the measured reduction of the iron solution. A plot of percentage reduction of Fe^{+++}. against percentage.

TABLE 11.

Percentage Reduction of Fe^{+++}	E_∞	Percentage Difference in E_∞
0	0.770	0
6.4	0.705	7.1
11.0	0.681	11.5
13.7	0.058	14.5
18.5	0.641	16.8
23.6	0.609	21.2
23.9	0.607	21.2

decrease in E_{∞} is shown in Fig. 38. The dotted line is the theoretical relation and the excellent experimental agreement found confirms the explanation given above as to the shape of the hydrolysis curves.

The marked influence of p_H on the appearance and rate of hydrolysis is evident on comparing Figs. 4 and 39 (p_H's 3.05 and 2.95 respectively). Fig. 39 also shows the progress of hydrolysis in the dark after the removal of the solution from the light source in one case at time (a), and in another at time (b), the subsequent dark hydrolysis being shown by curves 1 and 2 respectively. It is thus easily seen that the total remaining ferric iron in the solution decides the maximum optical density.

It can therefore be inferred that the important function of the light is the initiation of the hydrolysis. Subsequent removal of the solution from the light source has little effect on the rate of hydrolysis although the longer the exposure the smaller is E_{∞}, readily understood.

The effect of light is not always to accelerate hydrolysis as a study of the effect of temperature indicated (Figs. 40,41). At 12°C. and 20°C. light accelerates the hydrolysis whereas at 25°C. and 30°C.

FIG. 38.

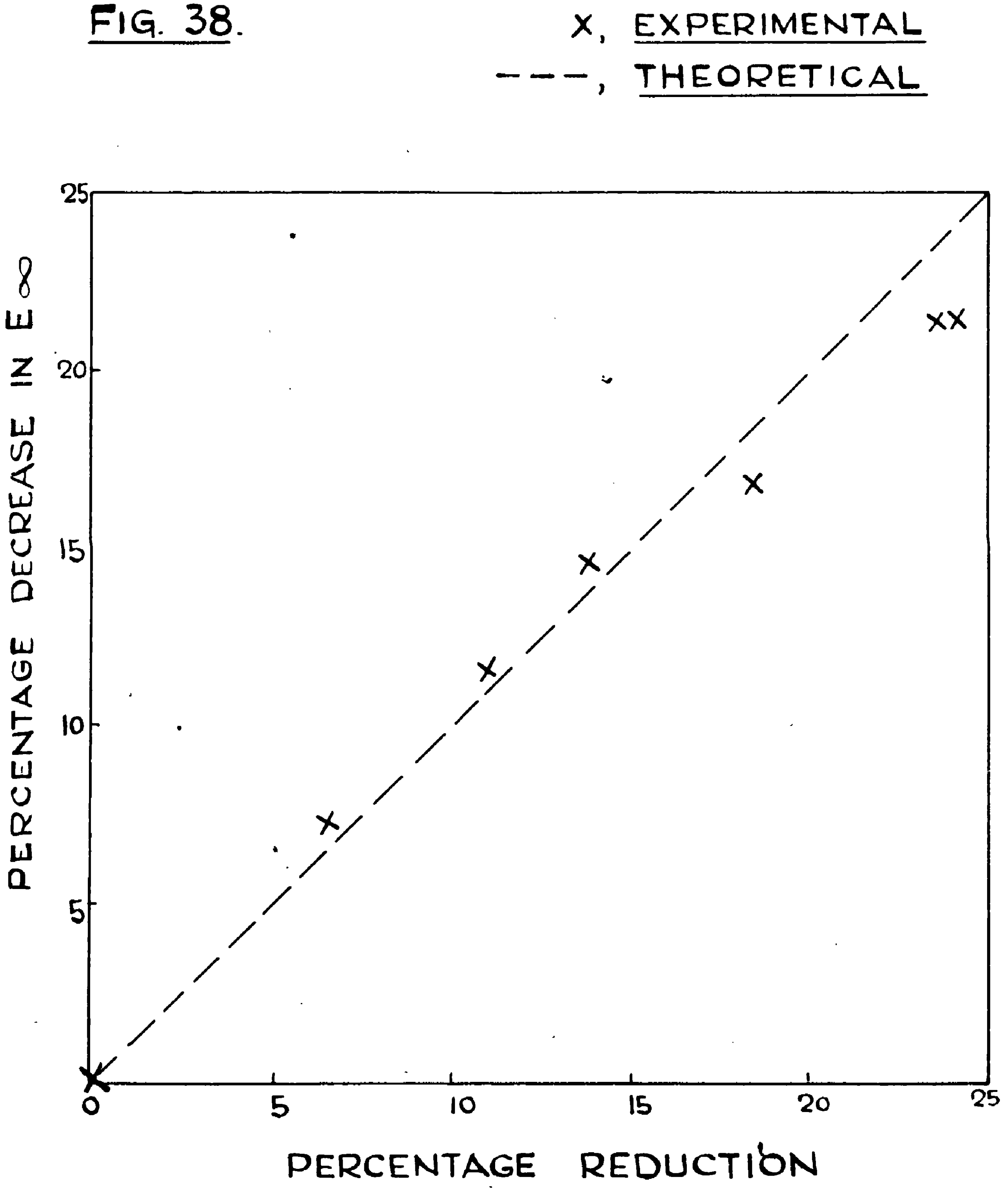
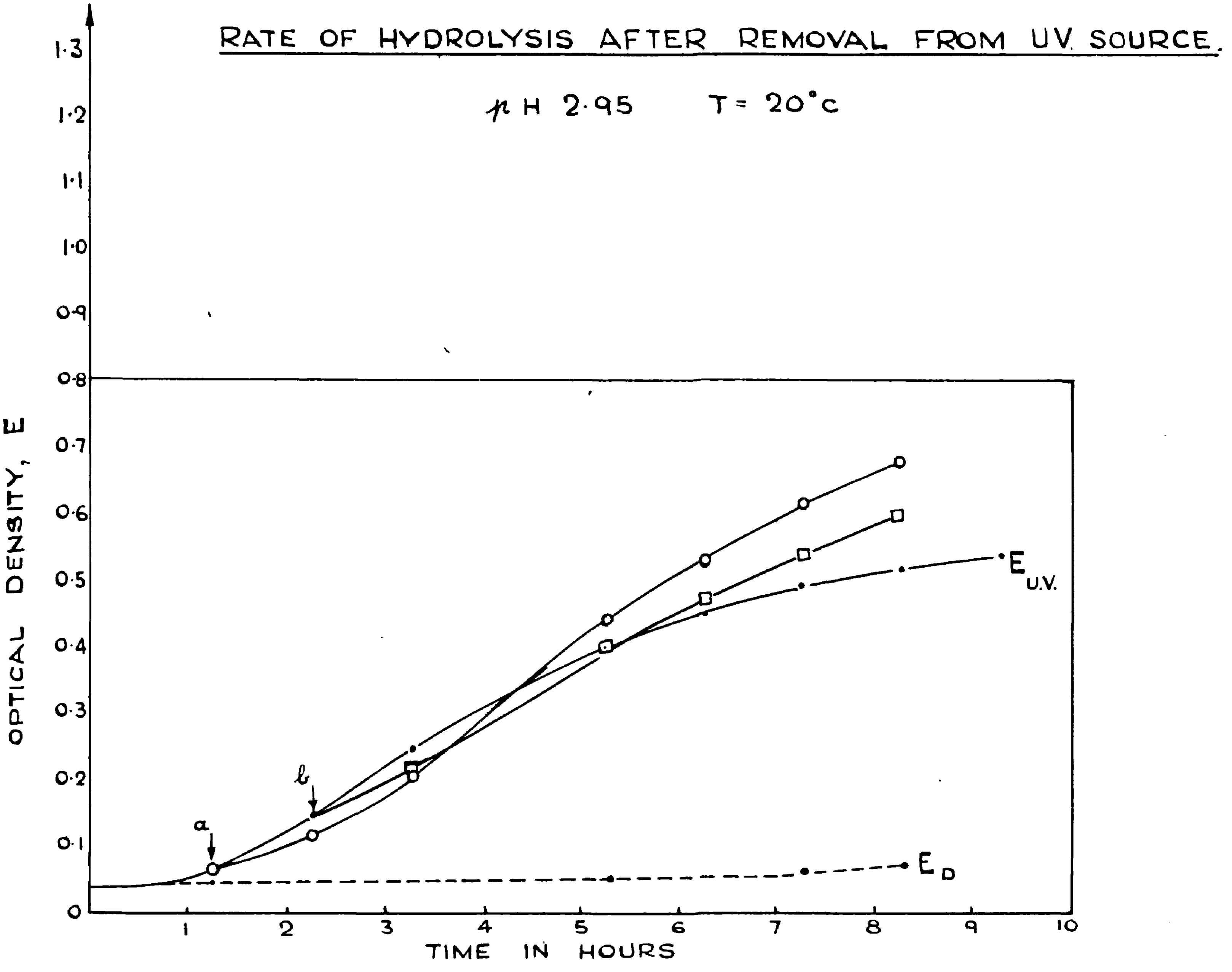

X, EXPERIMENTAL
---, THEORETICAL
PERCENTAGE DECREASE IN E∞
PERCENTAGE REDUCTION
0
5
10
15
20
25
5
10
15
20
25

FIG. 39.

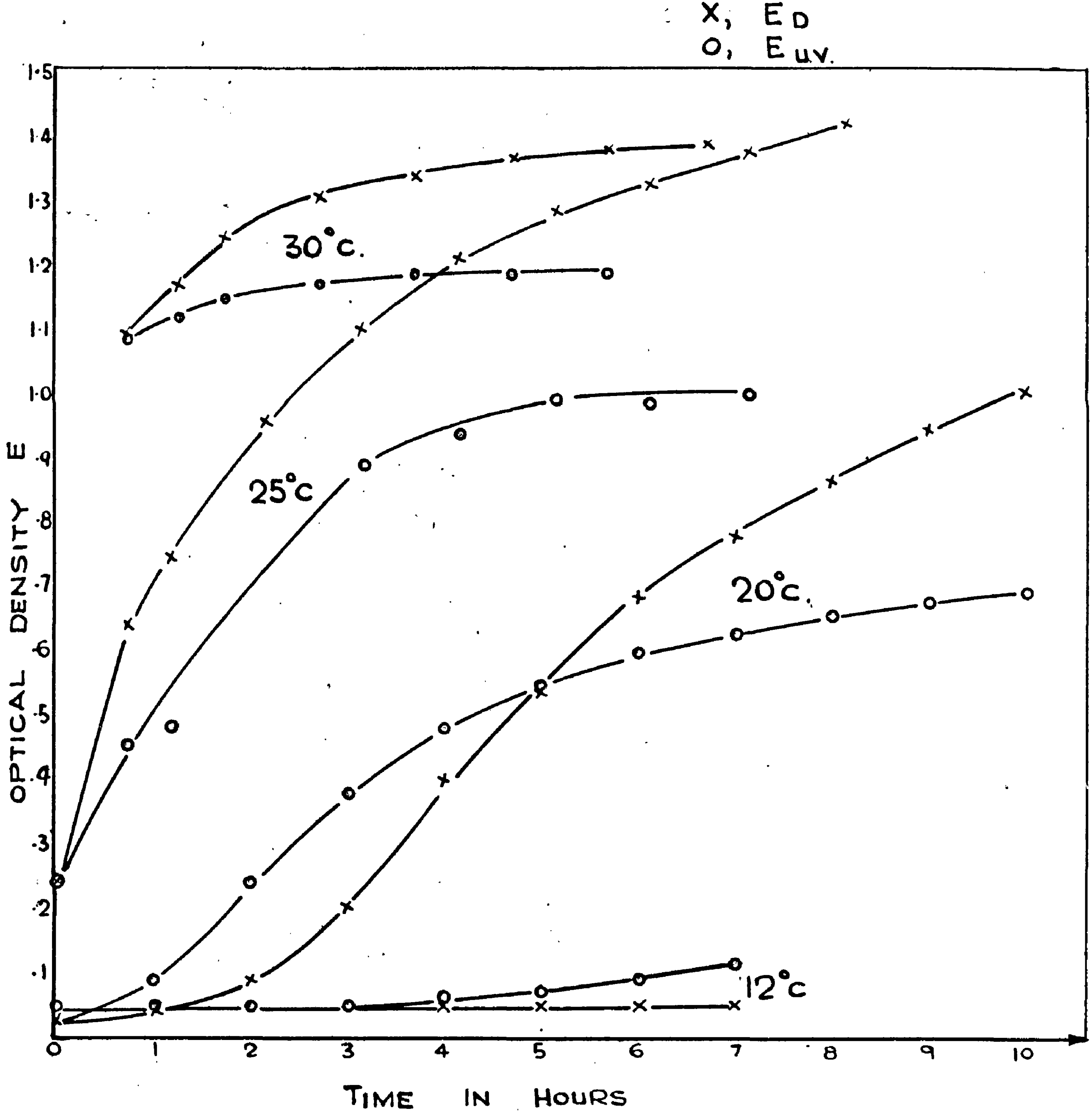


RATE OF HYDROLYSIS AFTER REMOVAL FROM U.V. SOURCE.

pH 2·95 T = 20°c

FIG. 40

VARIATION OF E_D AND E_{UV} WITH TIME AT DIFFERENT TEMPS. $pH = 3.05$



the light retards it.

It is to be noted however that at the two lower temperatures the hydrolysis is actually initiated by the light whereas at the higher ones hydrolysis is well advanced before exposure.

A similar retarding action is shown by an ageing 87 solution (Fig. 10, ~~[illegible]~~). Here at age zero light accelerates the hydrolysis,but at age 24 hours and 48 hours where initiation has taken place in the dark, light retards it. It should be noted that at age 24 hours hydrolysis in the dark <u>has just begun</u>. This is strong evidence that the action of light is to initiate hydrolysis.

It is probable that the retardation found when solutions are exposed after hydrolysis has begun is due to the ensuing decreasing ferric iron concentration in the exposed solutions. E_∞ must inevitably lie below that of the 'dark' solutions.

(B). The Effect of Decreased Ferric Iron Concentration.

Lamb and Jacques have shown that the rate of hydrolysis of ferric iron is an inverse function of the concentration, i.e. the smaller the concentration the smaller is the induction period prior to hydrolysis and the faster is the rate of the subsequent hydrolysis.

With the irradiated system here the concentration of ferric iron is continually falling. Considering pH 3.05, the initial concentration of $1.30 \times 10^{-3}\bar{M}$ ferric falls to $1.02 \times 10^{-3}\bar{M}$ with a three hour exposure at 20°C. There was a possibility that the initial acceleration of the hydrolysis was simply due to this factor.

The rates of hydrolysis at 20°C., in the dark of $1.3 \times 10^{-3}\bar{M}$, $1.17 \times 10^{-3}\bar{M}$ and $1.04 \times 10^{-3}\bar{M}$ ferric chloride at p_H 3.05 were compared with that of $1.3 \times 10^{-3}\bar{M}$ exposed to U.V. light.

The results shown in Fig. 41 indicated the possibility of some relation.

But when the experiment was repeated at a lower p_H of 2.80, which of course shows a longer induction period in the dark, it was evident that there was little connection between decrease of ferric ion concentration and the acceleration of hydrolysis with light (Fig. 42). Since hydrolysis had not even begun in the three 'dark' iron solutions after 22 hours whereas the one exposed for about 6 hours and then thermostated in the dark shows very condiserable hydrolysis after 22 hours.

FIG. 41. INFLUENCE OF CONCENTRATION OF Fe^{+3} ON HYDROLYSIS IN THE DARK.

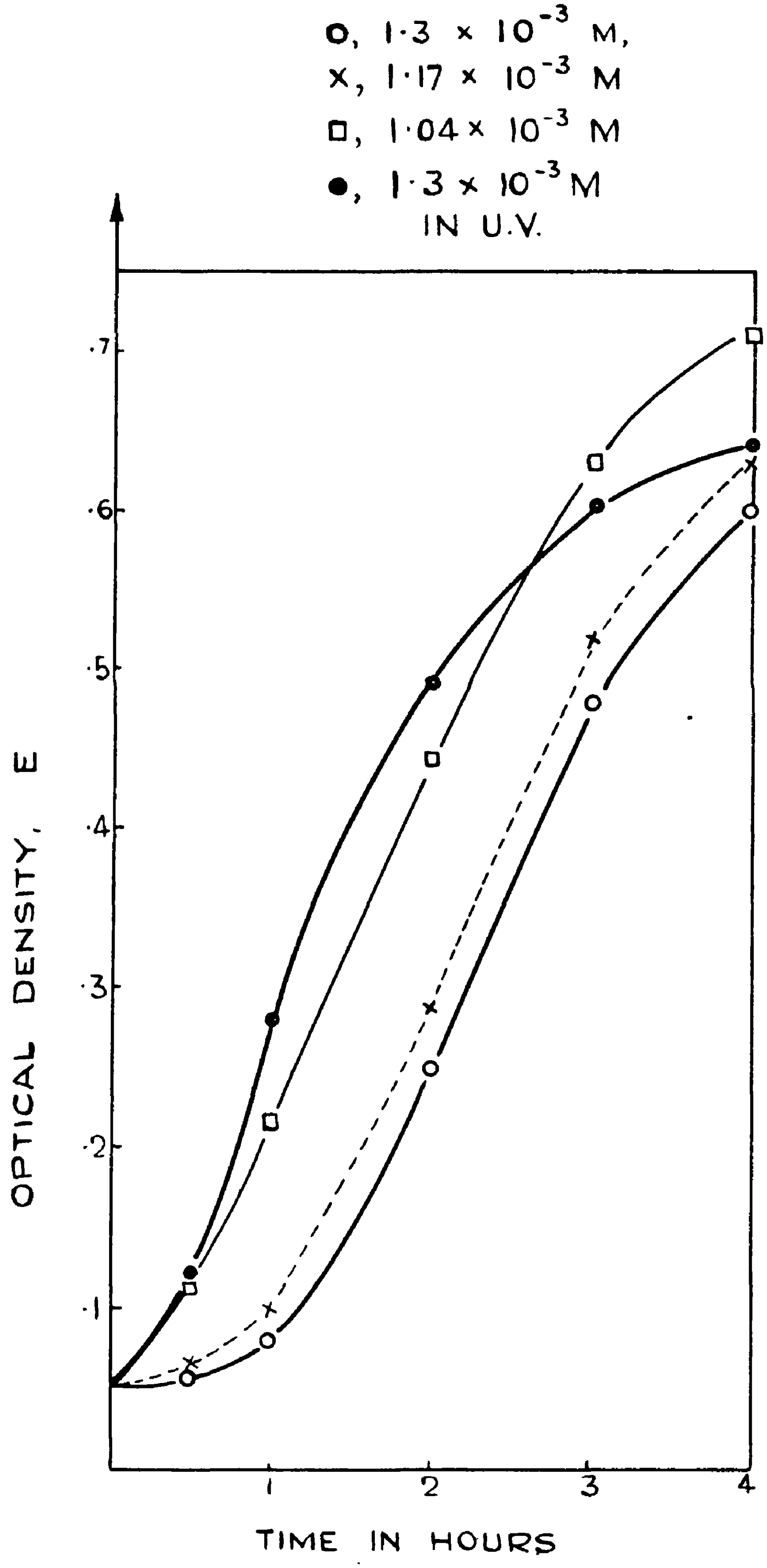
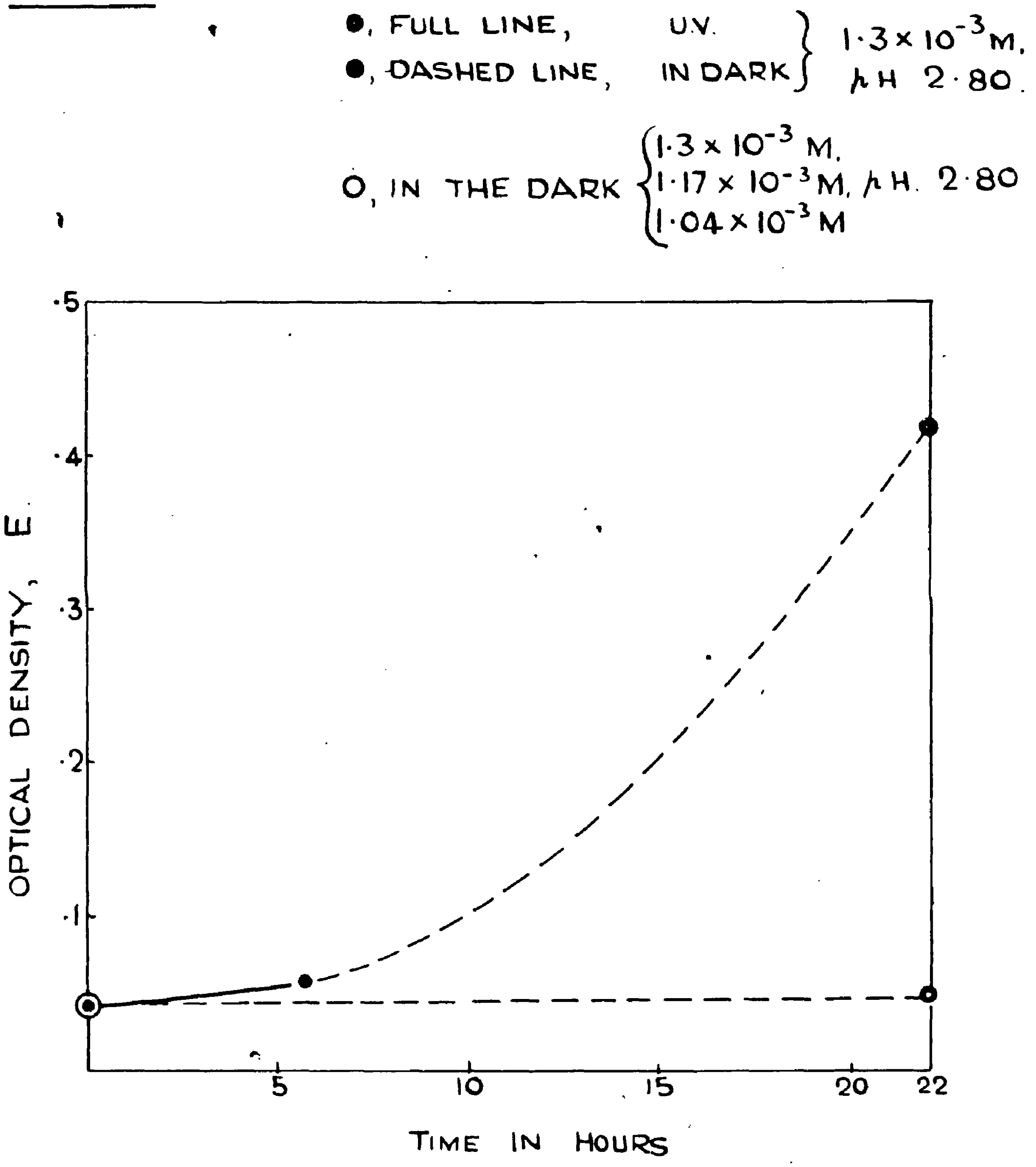


FIG. 42.


●, FULL LINE, U.V.
●, DASHED LINE, IN DARK
1·3 × 10⁻³ M, pH 2·80.
O, IN THE DARK
1·3 × 10⁻³ M.
1·17 × 10⁻³ M, pH 2·80
1·04 × 10⁻³ M
·5
·4
·3
·2
·1
OPTICAL DENSITY, E
5
10
15
20
22
TIME IN HOURS

(C). The Effect of Added Ferrous Ion.

The ferrous ion was added as chloride, and in amount about equal to that which might be formed in a photo-reduction. The ferric concentration was kept constant at $1.3 \times 10^{-3}\bar{M}$ and T = 20°C.

The effect of initially added ferrous ion on the dark hydrolysis at p_H 3.05 is shown in Fig. 43.

It is seen that if anything the ferrous iron has a slight retarding action.

However, when the same system is exposed to U.V. light for 40 minutes then thermostated in the dark, the initially added ferrous ion is seen to partially suppress the accelerating effect of light previously noted, and the higher the initial Fe^{++} concentration, the greater the suppression (Fig. 44).

The same effect is shown again in Fig. 45 where identical Fe^{+++} Fe^{++} ratios were studied, but at the slightly lower p_H of 2.95 at which 'light' hydrolysis starts a little later.

(D). The Addition of Substrate Glucose.

Again $[Fe^{+++}]_0 = 1.3 \times 10^{-3}\bar{M}$ throughout and

T = 20°C.

FIG. 43. THE EFFECT OF Fe^{++} ON HYDROLYSIS IN THE DARK. OF $1{\cdot}3 \times 10^{-3}$ M Fe^{+3} AT pH. 3·05. T = 20° C.

(1) no Fe^{+2}

(2) $6{\cdot}5 \times 10^{-5}$ M Fe^{+2} } ADDED BEFORE DILUTION.
(3) $1{\cdot}3 \times 10^{-4}$ M Fe^{+2} }

(4) $6{\cdot}5 \times 10^{-5}$ M Fe^{+2} } ADDED AFTER DILUTION.
(5) $1{\cdot}3 \times 10^{-4}$ M Fe^{+2} }

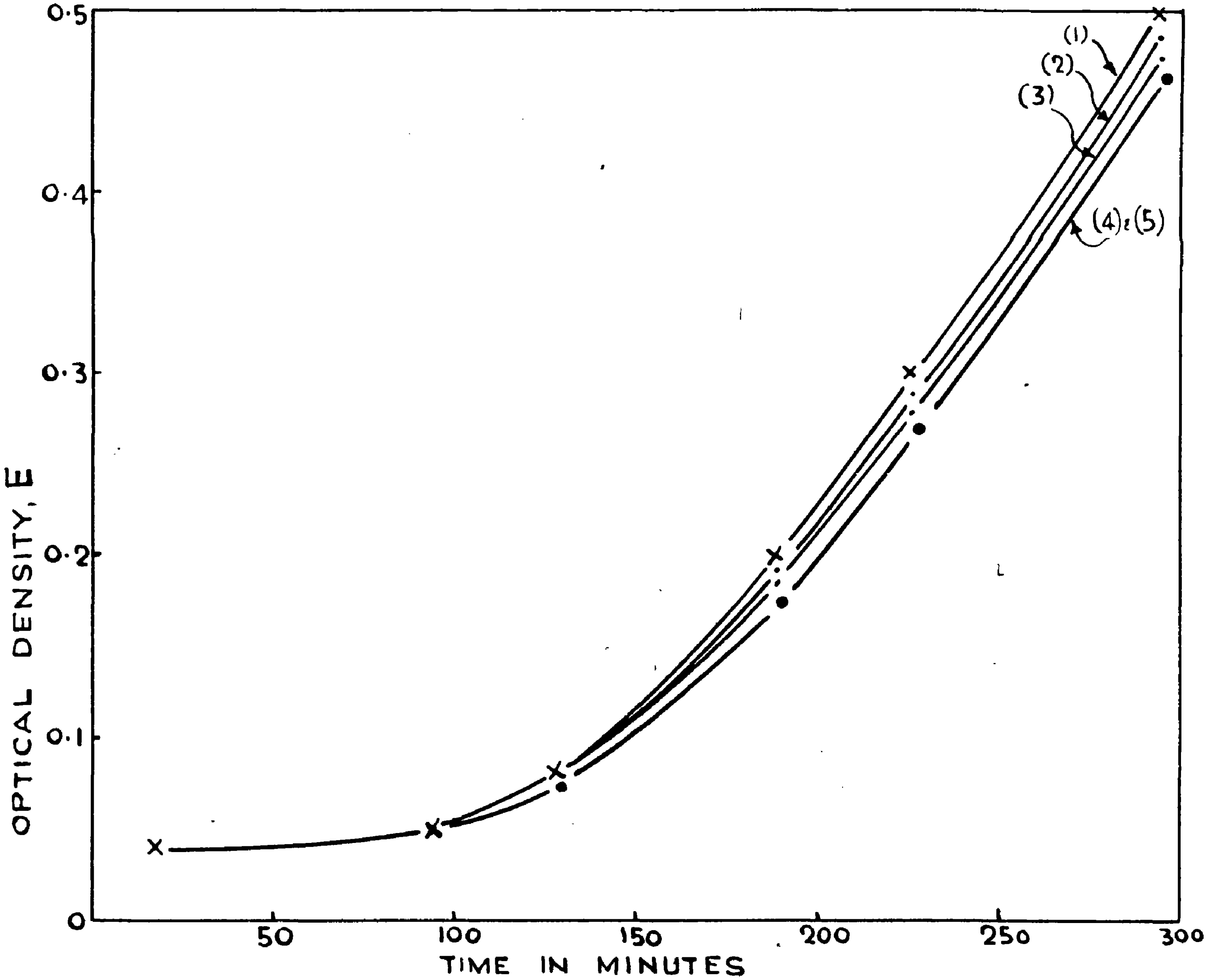


FIG. 44. THE EFFECT OF INITIALLY ADDED Fe^{++} ON.

HYDROLYSIS INITIATED BY LIGHT.

$Fe^{+3} = 1.3 \times 10^{-3}$ M $pH = 3.05$

(1) $Fe^{+2} = 0$, 40 MINS. EXPOSURE TO U.V.
(2) $Fe^{+2} = 6.5 \times 10^{-5}$ M EXPOSURE TO U.V.
(3) $Fe^{+2} = 1.3 \times 10^{-4}$ M EXPOSURE TO U.V.
(4) $Fe^{+2} = 0$, NO EXPOSURE

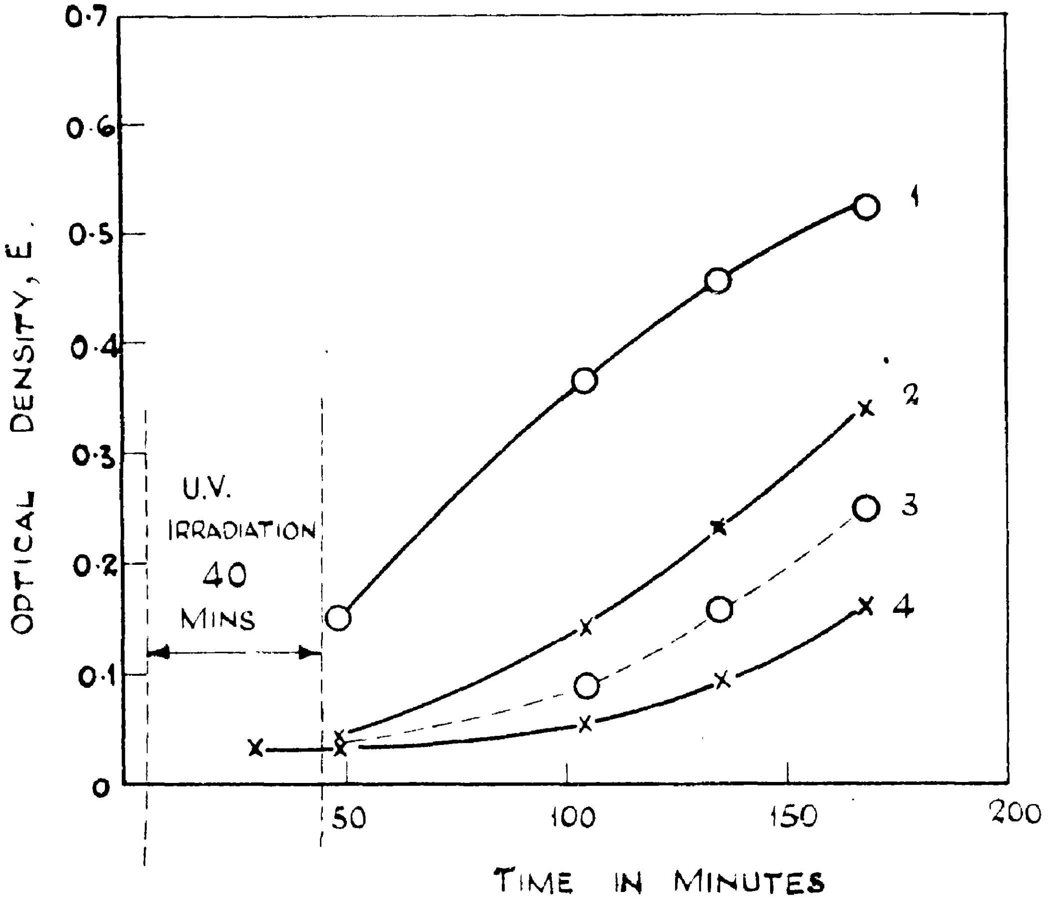
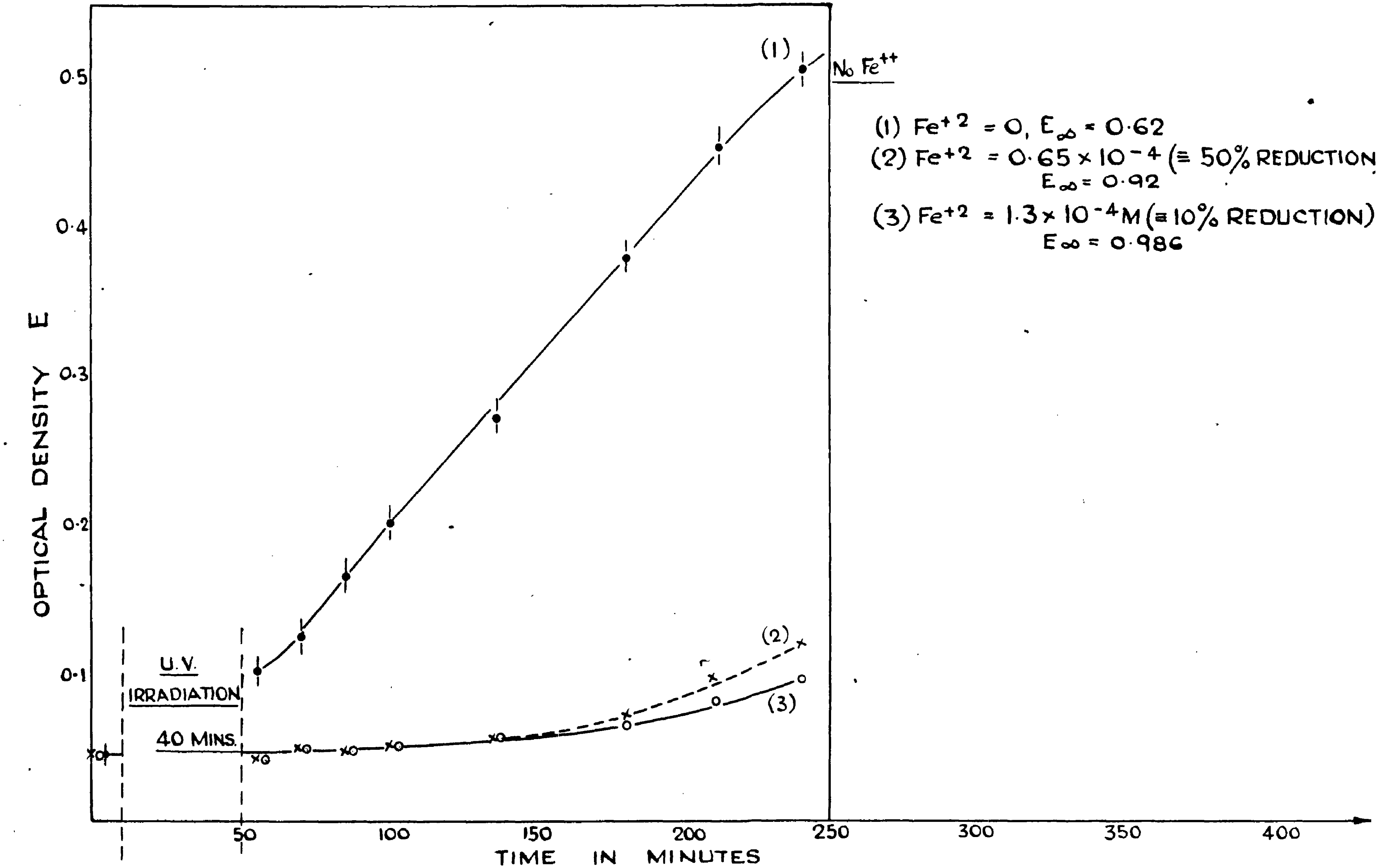


FIG. 45. HYDROLYSIS INDICATED BY LIGHT $Fe^{+3} = 1{\cdot}3 \times 10^{-3}$ M, pH = 2·95



An iron/glucose ratio of 100/1 was chosen and it was shown that the organic substrate had no effect on the dark hydrolysis at the glucose concentration used.

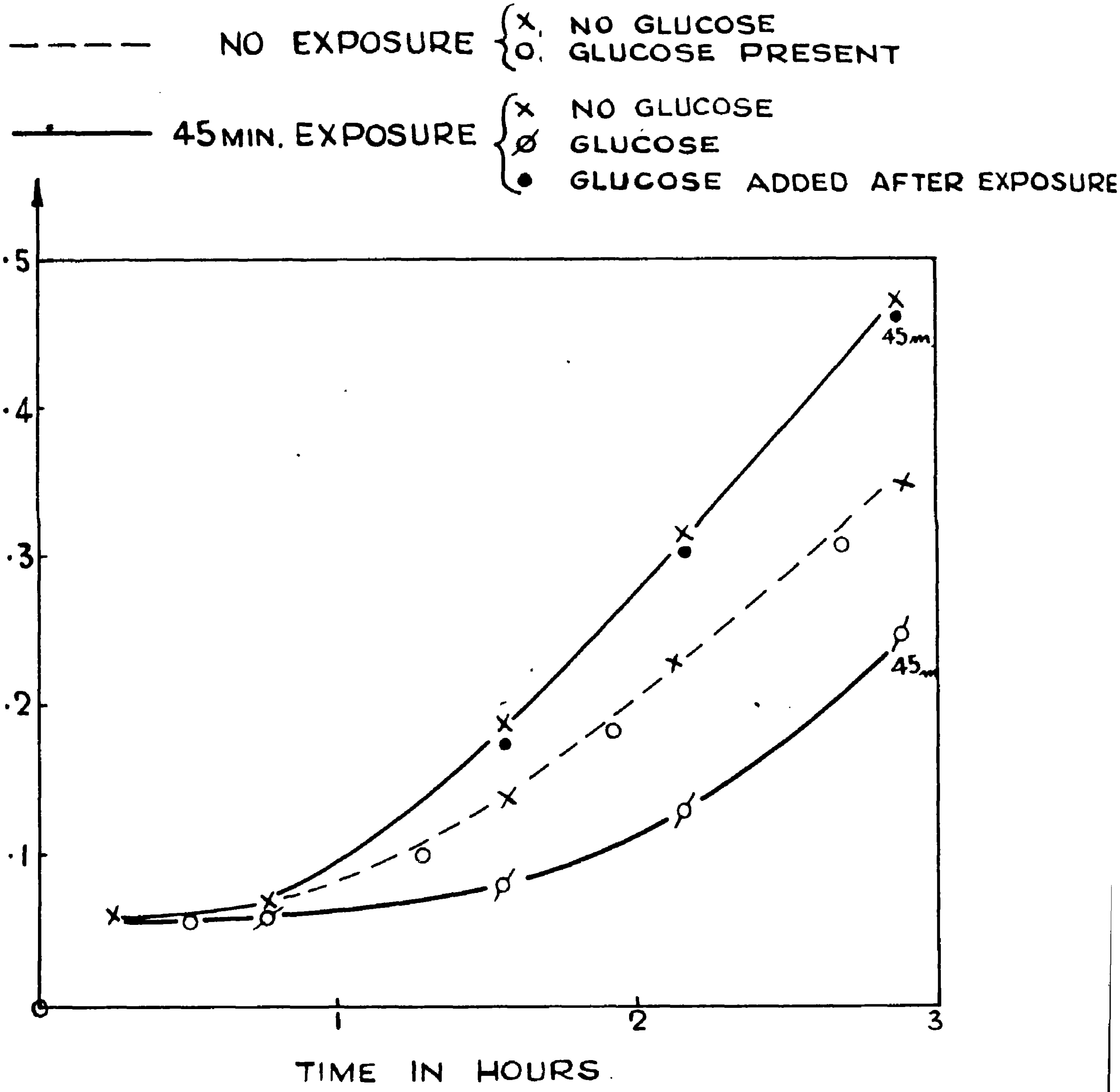
The systems iron and iron/glucose were then given a 45 minute exposure by a 200 watt tungsten lamp and subsequent hydrolysis followed in the dark. The effect of exposing an iron solution with the addition of glucose made after the exposure was also determined. The results are shown together in Fig. 46. It is seen that the concentration of glucose used has no effect on the dark hydrolysis. When the solution with no added substrate is exposed to light the hydrolysis is accelerated as expected. The solution containing glucose however does not show the accelerating effect, indeed the hydrolysis is retarded below that of the normal dark hydrolysis. Glucose added after exposure has no influence on the subsequent hydrolysis.

(E). The Reaction $Fe^{++} + H_2O_2$.

It was decided to investigate the effect of the oxidation of Fe^{++} by H_2O_2 on the dark hydrolysis.

A $5 \times 10^{-3}\bar{M}$ ferrous chloride solution was prepared and portions diluted to the required ferrous

FIG. 46. EFFECT OF GLUCOSE ON LIGHT INITIATED HYDROLYSIS.



concentration. The ferric salt was diluted into this ferrous solution, the ferric concentration being such that on oxidation of the ferrous ion by H_2O_2 the total ferric in each solution would be the same, $1.3 \times 10^{-3}\bar{M}$, and if p_H 2.95. A stock $5 \times 10^{-2}\bar{M}$ H_2O_2 solution was prepared from Laporte's 80% A.R. H_2O_2 (unstabilised). Both the ferrous and H_2O_2 solutions were standardised with potassium permanganate solution (Zimmerman-Reinhardt's solution being used with Fe^{++} as Cl^- present).

A volume of 500 ml. of the Fe^{+++}/Fe^{++} system was used for oxidation and twice the stoichiometric amount of H_2O_2 was added with vigorous stirring.

The experiments were carried out at 20°C. in blackened flasks. Table 12 gives the details of the molarities of the solution used.

TABLE 12.

Oxidation of Ferrous Iron.

Initial Fe^{+++} $\times 10^3$	Added Fe^{++} $\times 10^3$	Vol. 0.05 $\bar{N}$ H_2O_2 added to 500 ml. solution.	Final Fe^{+++} $\times 10^3$
1.3	0	0	1.3
1.24	0.06	1.3	1.3
1.17	0.13	2.6	1.3

It was found (Fig. 47) that the dark hydrolysis was markedly accelerated by this reaction, the effect being more pronounced as the concentration of 'oxidised' Fe^{++} was increased.

(F). The System Ferric/Hydrogen Peroxide.

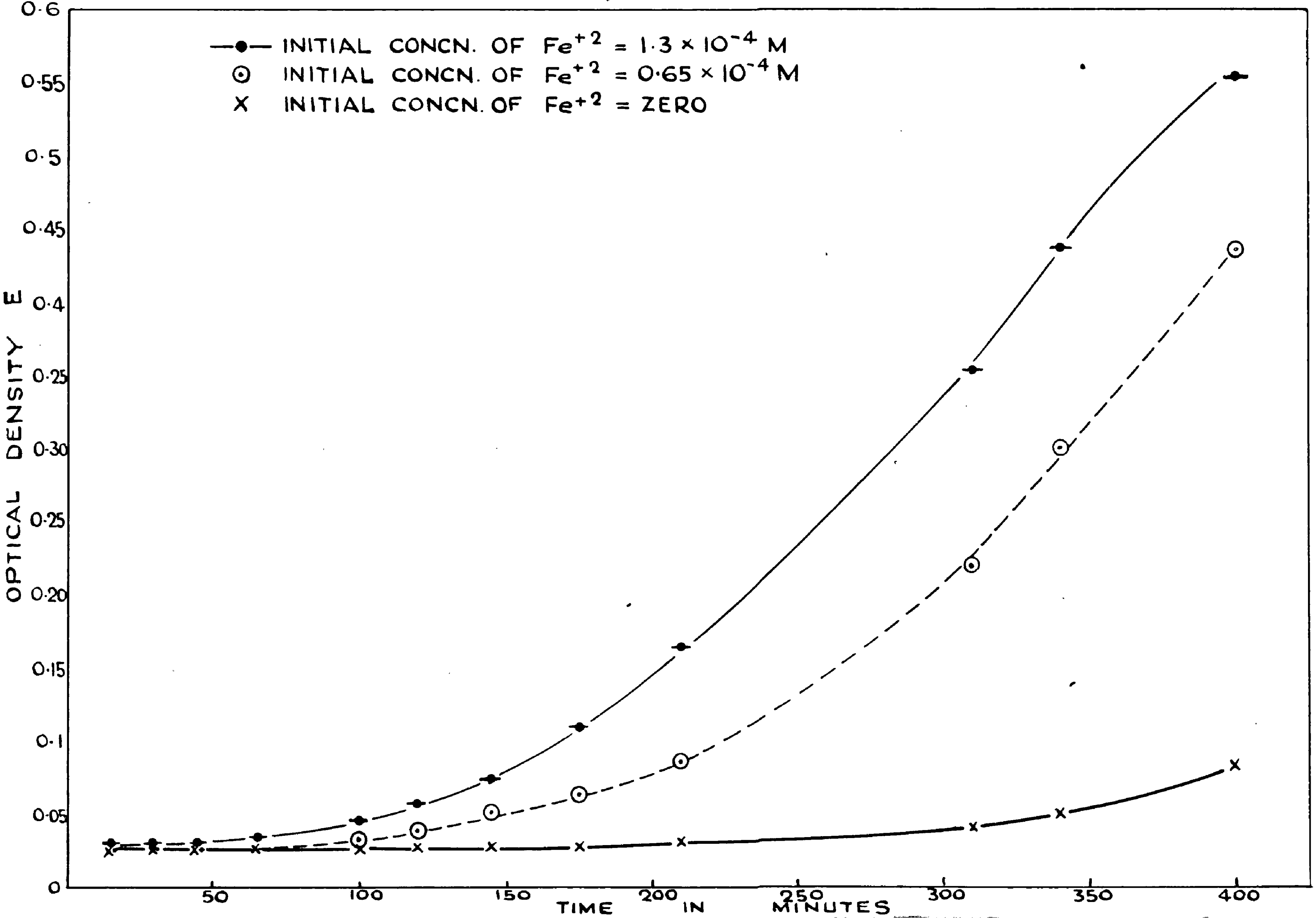
It had been noted in earlier work on the decomposition of hydrogen peroxide by ferric iron (Part 4 of this thesis) that the secondary hydrolysis of the iron solution in the presence of hydrogen peroxide took place earlier than one without peroxide, the hydrolysis being detected by the formation of the reddish-brown colour of ferric hydroxide.

Evans, George and Uri[17] investigated the deep brown colour in aqueous solutions of ferric ions and concentrated hydrogen peroxide, and postulated the colour was due to the complex $Fe^{3+}HO_2^-$. A later discussion shows that the concentration of this complex is too small in the present system to make any contribution to the brown colour found here, and consequently colour formation is attributed to hydrolysis.

---

[17] Evans, George and Uri, Trans.Farad.Soc., 1949, 45, 230.

FIG. 47. THE EFFECT (ON HYDROLYSIS) OF THE OXIDATION IN SITU OF FERROUS IRON.



The concentration of ferric chloride was $1.3 \times 10^{-3}\bar{M}$ as before while two concentrations of H_2O_2 were used, 1.25 $\bar{N}$ 40 and 3.12 $\bar{N}$ 40. The p_H was 3.05 and temperature 20°C.

The reaction was carried out in blackened flasks, samples being withdrawn by pipette at noted time intervals for optical density measurements. The samples were not returned to the flask. The rate of decomposition of the H_2O_2 was followed by titrating samples with standard permanganate solution.

The strange form of hydrolysis curve obtained in peroxide solution is shown in Fig. 48. Soon after the peroxide was added (to give a 2.5 $\bar{N}$ 40 solution), hydrolysis began, starting rather slowly at first and followed by a very sudden acceleration. This acceleration quickly disappears and the hydrolysis of the non-peroxide solution caught up, after which the hydrolysis in both solutions proceeded at the same rate, the peroxide one being a little ahead.

Fig. 49 shows the same effect only this time the peroxide solution was added a little later, when the solution was beginning to hydrolyse. It is seen that the boost in hydrolysis starts earlier.

FIG. 48. THE EFFECT OF H_2O_2 ON HYDROLYSIS.

O, H_2O_2 CONCN. (INITIAL) = 1·25 N/40, E_∞ = 1·45

X, NO H_2O_2, E_∞ = 1·40

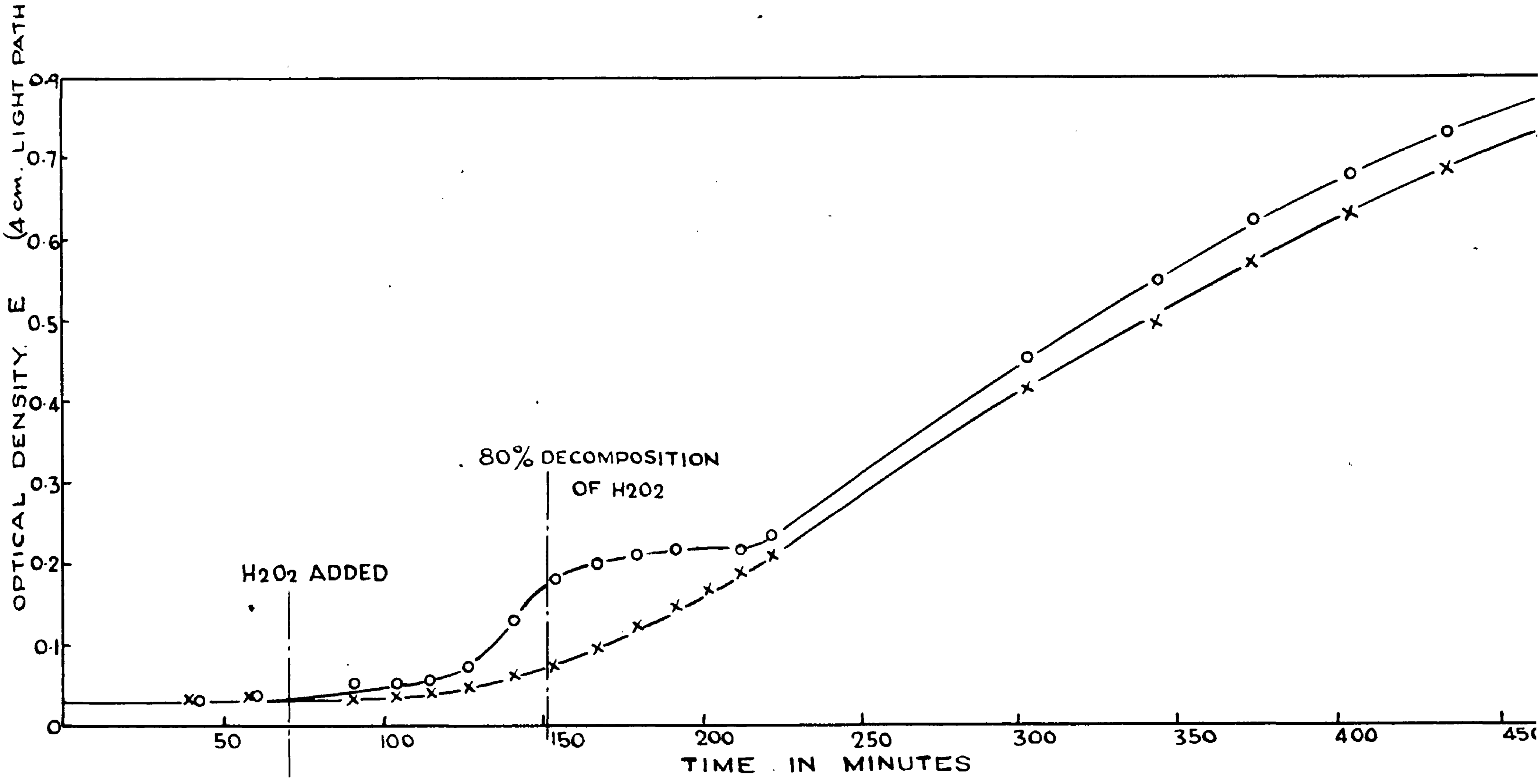
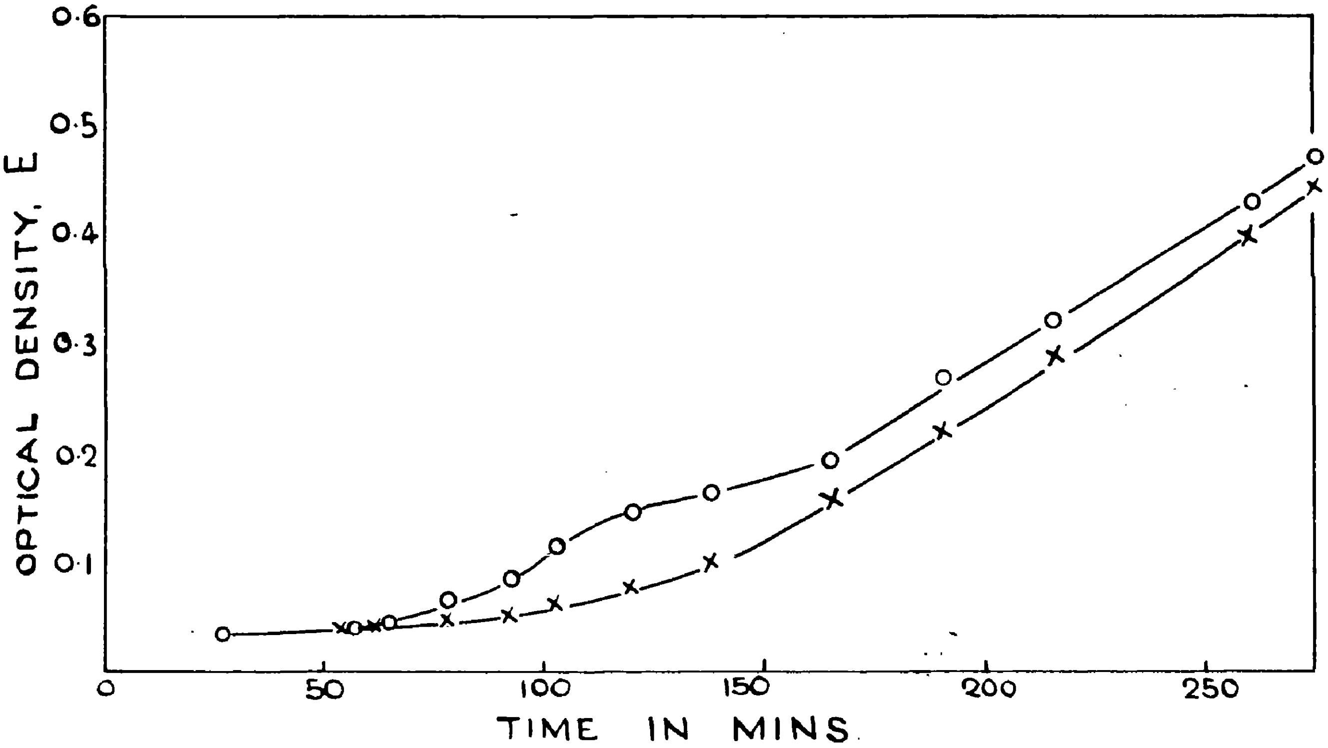


FIG 49. THE EFFECT OF H_2O_2 ON HYDROLYSIS

X, $[Fe^{+++}] = 1{\cdot}3 \times 10^{-3}\bar{M}$. T_2 20°C. pH^2 3·05 NO PEROXIDE.

O, $[Fe^{+++}] = 1{\cdot}3 \times 10^{-3}\bar{M}$ T_2 20°c pH^2 3·05 INITIAL $[H_2O_2]_2$ $1{\cdot}25\frac{N}{40}$



The effect of adding peroxide to a solution whose hydrolysis was under way is seen in Fig. 50. The instantaneous boost is evident. An increase in H_2O_2 concentration (of approximately 2½ times) gives evidence of an even bigger initial boost in hydrolysis as shown in Fig. 51. However the dark hydrolysis seems to have a greater speed than usual. A new stock $FeCl_3$ happened to have been used here. The discrepancy was not investigated further.

(G). Initiation of Hydrolysis by Seeding.

Secondary hydrolysis is attributed to the breakdown of the supersaturated condition of $Fe(OH)_3$ in solution[4]. The results given below show that this supersaturation can be broken by artificial 'seeding' on addition of a small quantity of colloidal ferric hydroxide solution. It is shown that the more numerous the 'seeds' the faster is the initial rate of hydrolysis.

This effect was first demonstrated by Goodwin[16].

The colloidal solution used was a $1.3 \times 10^{-3}\overline{M}$ ferric chloride solution of p_H 3.05 that had been aged 24 hours at 20°C. Hydrolysis was complete as shown by the E_∞ value although the solution showed only a

---

[16] Goodwin, Z.Physik.Chem., 1896, 21, 1. (see Ref. 1,pt.1)

FIG 50. THE EFFECT OF H_2O_2 ON HYDROLYSIS.

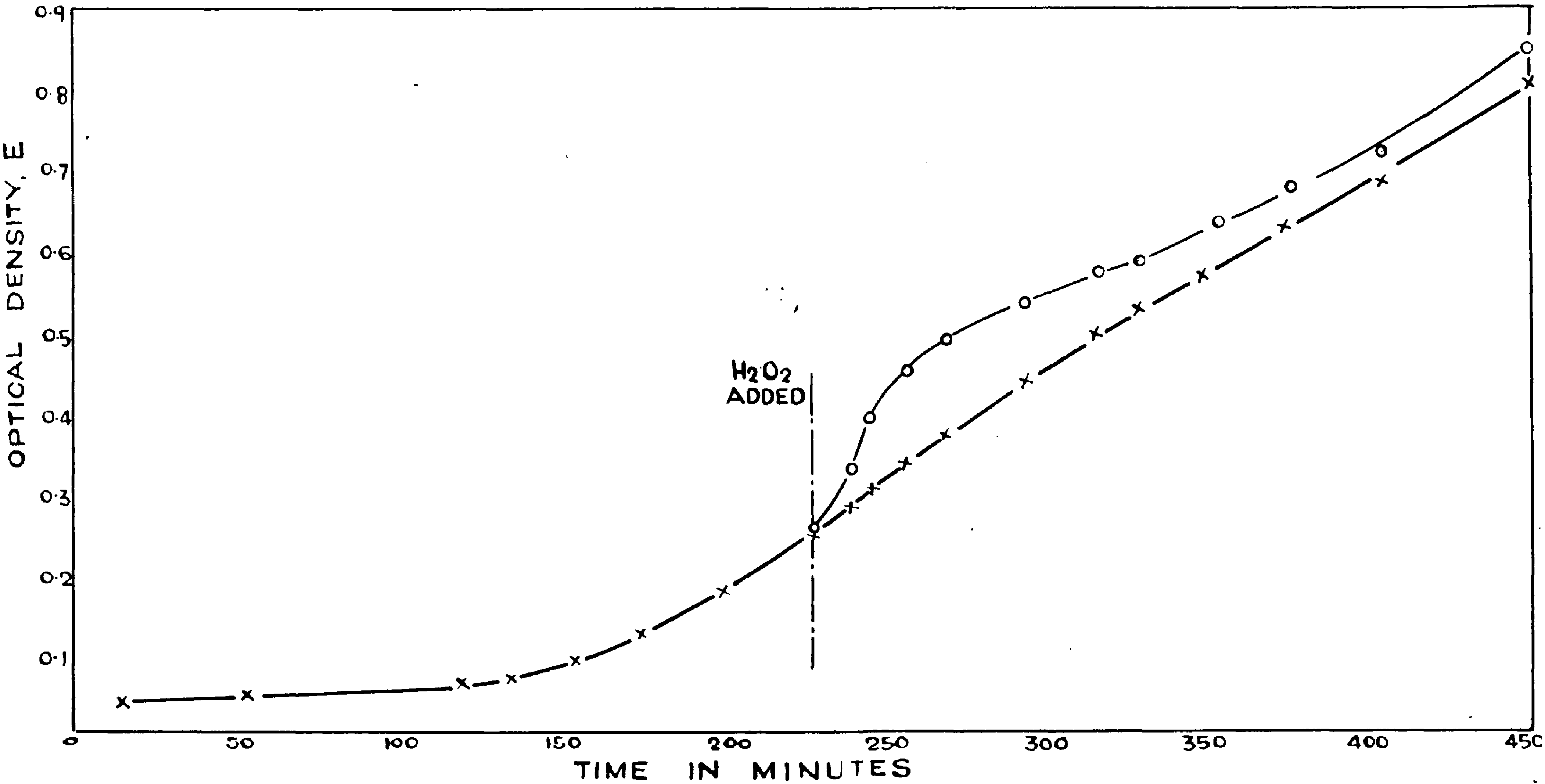
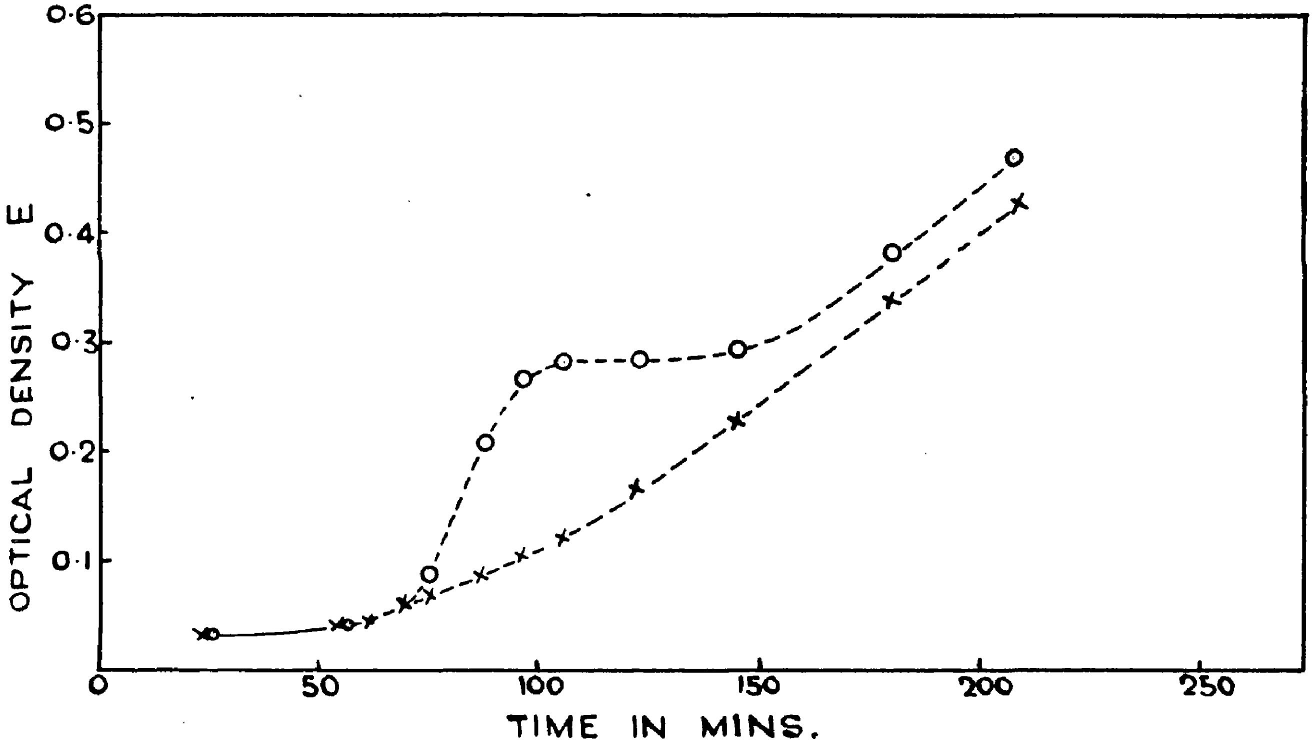


FIG. 51. THE EFFECT OF H_2O_2 ON HYDROLYSIS

X, NO PEROXIDE

O, $[H_2O_2] = 2\frac{1}{2} \times (1 \cdot 25 \frac{N}{40})$

Fe^{+++} SOLUTION AS IN FIG. 49 BUT PREPARED FROM A NEW STOCK OF $FeCl_3 . 6H_2O$.



slight 'Tyndall' cone when a beam of light was passed through.

The solution, whose initial rate of hydrolysis was being investigated, was 1.3 x $10^{-3}\overline{M}$, p_H 3.05, zero age.

Table 13 gives the volumes of the 'seeding' solution added to 500 ml. of this solution. Final volumes were adjusted so that the initial ferric concentration was the same in each solution (neglecting added colloidal ferric hydroxide).

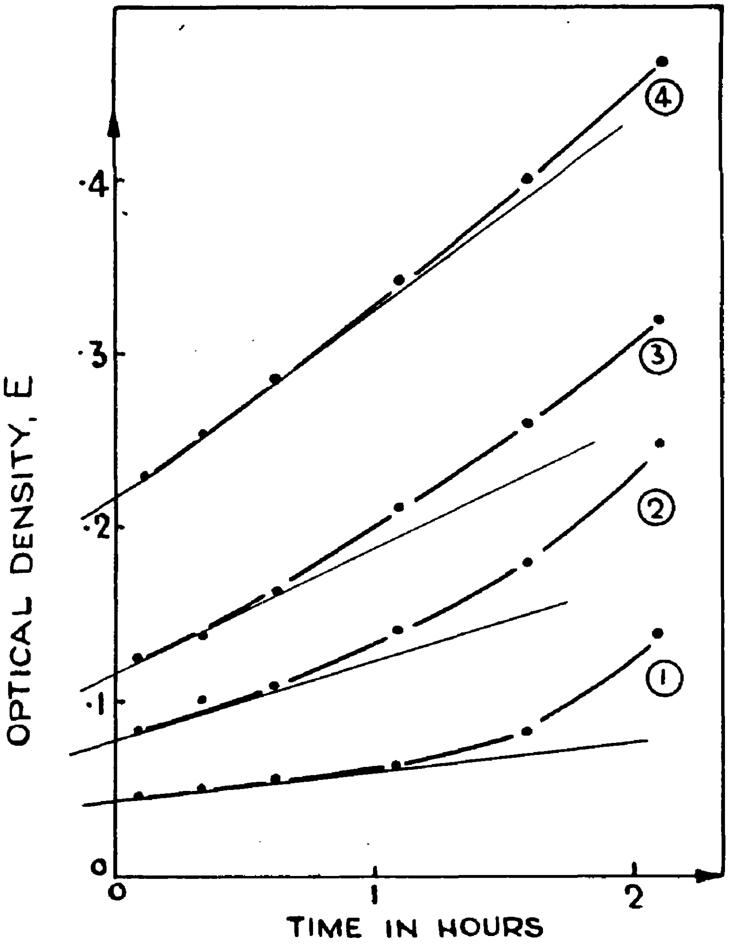
TABLE 13.

Solution	Vol. in Mls. Colloidal $Fe(OH)_3$/500 ml. Soln.	Initial Rate of Hydrolysis. $\frac{dE}{dt}$
1	0	0.15
2	10	0.45
3	20	0.75
4	50	1.1

Graph 52 shows the early stages of the hydrolysis. The initial values of the optical density (E) are of course different for each solution because of the different volumes of brown ferric hydroxide solution added, but the initial rates of hydrolysis calculated as $\frac{dE}{dt}$ and shown in Table 13 indicate the pronounced seeding effect of the added solution.

FIG. 52. THE EFFECT OF $Fe(OH)_3$ SEEDING ON HYDROLYSIS.

CURVES 1, 2, 3, 4, CORRESPOND WITH SOLUTIONS IN TABLE 13.



Discussion.

Light of 365 mμ is active in causing the acceleration of hydrolysis by light (see Part 3).

It is accepted that the following reaction scheme describes the photo-reduction of the ferric iron under the conditions of the present investigation. (The Hanovia lamp, unfiltered, was the light source).

$$\mathrm{Fe^{+2}(OH)_2{}^{+4}} \xrightarrow[h\nu]{k_i} \mathrm{Fe^{+3}OH^- + Fe^{+2} + OH^- + OH} \ldots (1)$$

$$\mathrm{Fe^{+2} + OH} \xrightarrow{k_2} \mathrm{Fe^{+3} + OH^-} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\mathrm{Fe^{+3}OH^- + OH} \xrightarrow{k_3} \mathrm{Fe^{+2} + H_2O_2} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\text{or} \quad \mathrm{Fe_2(OH)_2{}^{+4} + OH} \xrightarrow{k_4} \mathrm{Fe^{+3}OH^- + Fe^{+2} + H_2O_2} \ldots\ldots (4)$$

$$\mathrm{Fe^{+2} + H_2O_2} \xrightarrow{k_5} \mathrm{Fe^{+3} + OH^- + OH} \ldots\ldots\ldots\ldots (5)$$

$$\text{Ferric} + \mathrm{H_2O_2} \longrightarrow \text{Ferrous} + \text{Oxygen} \ldots\ldots\ldots\ldots (6)$$

If an organic substrate, e.g. glucose is added to the system, then the reaction

$$\text{Glucose} + \mathrm{OH} \xrightarrow{k_7} \text{Products} \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

takes place.

Considering first the acceleration of the initiation of hydrolysis by light as shown for example in Fig. 4

the following points must be considered. (This acceleration is hereafter termed 'Accelerating Action').

(A). The Effect of Substrate Glucose.

Glucose has no effect on the 'dark' hydrolysis, but on exposure, the previously observed acceleration of hydrolysis in the absence of substrate is not evident, indeed the hydrolysis of the iron glucose U.V. system is slower than Fe Glucose dark.

c/ The effect of glu~~x~~ose on the photo-reduction is described by equation (7), i.e. its effect is twofold. -

- (a) It competes with reactions (2), (3) and (4) for the OH radical.
- (b) Formation of hydrogen peroxide in the presence of glucose is insignificant, for the effect of glucose concentration on photo-reduction (Fig. 11) suggests that $k_7 \gg k_2$ and consequently $k_7 \gg k_3$ and k_4.

Therefore it appears that the OH radical and or H_2O_2 may play some part in the 'Accelerating Action'.

(B). The Effect of Initially Added Ferrous Ion.

Ferrous ion has almost no effect on the 'dark' hydrolysis. However on irradiation initially added ferrous ion lessens the accelerating action observed in its initial absence. This could be due to reaction (2) or reaction (5) or both.

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

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

(C). The Reaction $Fe^{+2} + H_2O_2$ in the dark.

Ferrous ion was oxidised in the dark by H_2O_2 in the presence of ferric iron and subsequent hydrolysis followed.

The reaction accelerated the 'dark' hydrolysis, and the acceleration was directly dependent on the concentration of [oxidised Fe^{+2}].

It may then be said that the retardation, described in(B) above, with added Fe^{+2} is not due to the reaction

$$Fe^{+2} + H_2O_2$$

but more likely due to $Fe^{+2} + OH$. The acceleration shown on the addition of H_2O_2 to the ferrous ferric mixture could be based on the reaction

$$Fe^{+2} + H_2O_2$$

and or $Fe^{+3} + HO_2^-$

The latter reaction is considerably slower than the first[17] and this, together with the correspondence of [oxidised Fe^{+2}] and 'Accelerating Action', makes it very probably that this acceleration of hydrolysis with added H_2O_2 is based on the reaction $Fe^{+2} + H_2O_2$.

Assuming that this reaction between ferrous ion and hydrogen peroxide forms the basis of the 'Accelerating Action' <u>in the presence of light</u>, then the retarding effect of initially added Fe^{+2} described in B is readily understood.

Considering the reactions

$$Fe^{+2} + OH \xrightarrow{k_2} Fe^{+3} + OH^- \ldots\ldots\ldots\ldots\ldots(2)\ \Delta H = -59\text{k. cal.}$$

$$Fe^{+3}OH^- + OH \xrightarrow{k_3} Fe^{+2} + H_2O_2 \ldots\ldots\ldots\ldots(3)\ \Delta H = +(5\text{ to }7)\text{ k.cal.}$$

$$Fe_2(OH)_2^{+4} + OH \xrightarrow{k_4} Fe^{+3}OH^- + Fe^{+2} + H_2O_2 \ldots(4)$$

The heats of reaction indicate $k_2 > k_3$ and let us assume $k_3 \geqslant k_4$. Therefore the main effect of initially added ferrous ion would be to retard the formation of H_2O_2 (and the formation of Fe^{+2}; see Fig. 8).

Therefore if the reaction $Fe^{+2} + H_2O_2$ is the basis of the 'Accelerating Action' then it is expected that ferrous ion added before irradiation would repress this effect. This was found experimentally to be the case.

(D). The Reaction Ferric + H_2O_2 in the dark.

The catalytic decomposition of hydrogen peroxide by ferric ion was carefully studied by Barb, Baxendale, George and Hargrave[17], and it was shown that the deviation from first order decomposition, observed experimentally by Andersen[18], could be explained by assuming that the decomposition is a chain reaction produced by the small, but measurable, stationary concentration of ferrous ion.

i.e. in the Ferric peroxide system the reaction

$$Fe^{+2} + H_2O_2$$

takes place continuously.

Therefore from the above conclusions regarding the acceleration of hydrolysis by light, the system ferric/H_2O_2/dark should show a similar accelerating action.

This was found to be so as shown in Figs. 48,49,50 and 51. The strange shape of hydrolysis curve - initial boost followed by a 'flat' may be explained by assuming that on the addition of peroxide a multitude of ferric hydroxide nuclei form throughout the solution and hence a fast increase in extinction. With time however these nuclei coagulate into larger particles

---

[17] Barb, Baxendale, George and Hargrave, Trans.Farad.Soc., 1951, 47, 591.

and although the hydrolysis is proceeding, the absorption of light unit mass falls as the average particle size increases.

The deep brown colour of aqueous solutions of ferric ions and concentrated hydrogen peroxide was investigated by Evans, George and Uri[19]. The colour is attributed to $Fe^{+3}HO_2^-$. However the brown colour observed in the present work on ferric H_2O_2 systems is considered not to be due to this complex for two reasons.

(a) Although the concentration of ferric ion used is similar to that of Evans et al (10^{-4}-$10^{-3}\bar{M}$) the highest peroxide concentration used here is very much smaller than the range used in the work of Evans et al(5-33 $\bar{M}$). From their data on the effect of peroxide concentration on the optical density of the complex it is adduced that no colour formation in the present system due to $Fe^{+3}HO_2^-$ should be measurable.

(b) In some cases (Fig. 49) with the present system there is an induction period for colour formation on the addition of peroxide. No mention is made

---

18. Andersen, Acta.Chem.Scand., 1948, 2, 1.

19. Trans. Far. Soc., 1949, 34, 230

of this in Evan's work. It was found that the induction period was associated with the extent of the dark hydrolysis before the addition of the peroxide.

This discussion has been on the acceleration of the initiation of hydrolysis by light. However it has also been seen that if the hydrolysis has begun before exposure the light actually 'retards' the hydrolysis as measured by absorptiometry.

Therefore the action of light is twofold.

(a) Acceleration of initiation of hydrolysis, most likely due to the reaction $Fe^{+2} + H_2O_2$.

(b) 'Retardation' of the hydrolysis due to a decrease in $[Fe^{+++}]_{total}$ with photo-reduction, for E must necessarily be lower.

These two effects are directly opposing and the experimental conditions, e.g. temperature and age of solution, decide on which side the net effect lies. Generally speaking, if hydrolysis has not begun in the dark before exposure, the light accelerates the initiation of the hydrolysis, whereas if hydrolysis has begun, even to a small extent (Fig. 10) 'retardation' is observed.

The present experimental results are not sufficient to describe the mechanism of initiation of hydrolysis after the reaction $Fe^{+2} + H_2O_2$. Indeed the number of feasible reactions would probably never permit of a complete kinetic analysis. Nevertheless the following possibilities are suggested.

(a) $Fe^{+2} + H_2O_2 \xrightarrow{2H_2O} Fe(OH)_3 + OH + 2H^+$

i.e. the environment of the oxidised Fe^{+2} is such that complete hydrolysis takes place. A large increase in $[Fe(CH)_3]$ would probably break down the supersaturation of that species in solution.

(b) Coagulation of the small particles due to a clearance in the electrical double layer with a surface reaction. These larger 'seeds' will initiate the hydrolysis.

These results are contrary to the findings of Moore[9] who stated that light had no effect on hydrolysis. Under the experimental conditions coagulation of the solution once formed was very small, the solutions, though brown, remaining almost optically clear. The effect of light on coagulation observed by other workers[9,11,12,14,15] was not pursued. The presence of H_2O_2 in the system Ferric U.V. was suggested after the identification of oxygen as a reaction product.

This study of the effect of light on hydrolysis provides further, and independent evidence, that hydrogen peroxide is present.

====================

SUMMARY AND GENERAL CONCLUSIONS

Of Thesis By

William A. B. Purdon.

Solutions of 1.3×10^{-3}/M ferric chloride of ~~p_H~~ pH between 2.0 and 3.05, and in the absence of added substrate are found to be photo-active. The photo-activity is to be attributed to the 'dimer' $Fe_2(OH)_2^{+4}$ and possibly also to the species $Fe^{+3}OH^{-}$.

Experimental proof of OH radical formation is shown by the hydroxylation of substrates benzene and benzoic aci which are oxidised to phenol and salicylic acid respective

Experimental evidence is adduced to show that the photo-activity is not due to oxidisable organic impuritie in the distilled water. Possible processes are oxidation of chloride to chlorine and/or oxidation of water to oxygen.

No chlorine was found with a sufficiently sensitive test. In fact, irradiation of Fe^{+3}/Cl_2 solutions leads t the disappearance of chlorine.

Using the 'freezing and thawing' technique of Dain and Kachen for measurement of small quantities of gas, a non-condensible gas was found to be photo-produced in these iron solutions. The amount of gas was shown to accord with the stoichiometry of the equation:-

$$Fe^{+3} + \frac{1}{2}H_2O \longrightarrow Fe^{+2} + \frac{1}{4}O_2 + H^+$$

Further, the gas was identified as pure oxygen by

(a) the phosphor method of Kautsky and Hirsch,

(b) sparking with hydrogen, resulting in a 2 1 combination.

The photo-oxidation of water by ferric ion is thus established.

The following reaction scheme is proposed. -

$$Fe_2(OH)_2^{+4} \xrightarrow{h\nu} Fe^{+3}OH^- + Fe^{+2} + OH$$

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

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

or $OH + OH \longrightarrow H_2O_2$

and $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$.

iron
catalysis.

The quantum yield of Fe^{+2} formation

$$(\gamma_{Fe^{+2}})_{max.} = \cdot 026$$

Powdered silica was found to provide an active surface for the increase in photo-reduction of Fe^{+3}. In the analogous ceric cerous system Dain and Kachan suggest that the increased photo-activity is due to a recombination of OH radicals on the surface of the silica, leading to a higher oxygen yield.

It was shown in the present work that a 'fresh' surface of colloidal ferric hydroxide increases the photo-reduction of the iron. It is suggested that thi is due to some 'dark' heterogeneous reaction such as th recombination of OH radicals or catalysis of some elect -transfer reaction, which would in time increase the oxygen yield.

The effect of light intensity (365 mμ) was measure The initial $(\frac{dFe^{+2}}{dP}) \sim I$. However, the maximum yield i.e. $[Fe^{+2}]_{stationary}$ is a linear function of $\sqrt{I}$. Relatively high intensities are therefore necessary for easily measurable oxygen evolution, a suggestion alread made by Uri.

Light was found to initiate and accelerate the process of secondary hydrolysis of the iron to $Fe(OH)_3$, as compared with the dark hydrolysis. Experimental results point to the conclusion that the reaction, $Fe^{+2} + H_2O_2$ is basically responsible for the phenomenon and provide further, independent evidence that H_2O_2 is present in the system $Fe^{+3}/U.V.$