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ABSTRACT

The effect of sulphuric acid, ferrous and ferric ion, and oxygen concentrations on $G(Fe^{3+})$ values from cobalt-60 gamma-irradiated solutions has been studied. The ferrous sulphate concentrations ranged from $(1.0 \text{ to } 50.0) \times 10^{-3}M$ and the oxygen concentrations from 0 to $1.25 \times 10^{-3}M$ in three solvents: 1.0*M* sulphuric acid, 0.4*M* sulphuric acid, and 0.04*M* sulphuric acid/0.1*M* sodium sulphate solutions. Kinetic expressions were derived for reaction models involving reactions of various forms of the H atom and additional reactions postulated to be of importance at high solute concentration. Three models were assumed invoking the additional reactions: (1) an independent yield of an excited water species; (2) increasing contributions from interspur reactions of well established species at increasing solute concentration; (3) inhibition of charge pair recombination by acid and scavenger species. The calculated $G(Fe^{3+})$ values from the various models were compared by the least squares method with experimental $G(Fe^{3+})$ values from over 600 irradiations. Models 1 and 2 provided good fits to the data when an equilibrium $H_4O^+ \rightleftarrows H_3O^+ + H$ was assumed. The kinetic salt relationship for the results from model 1 gave partial support for a reaction involving a positively charged H atom species; those from model 2 indicated no significant participation of positively charged H atom species. Model 3 provided the best fit to the data for the least number of adjustable parameters. No evidence for more than one form of H atom was found with this model. The G value for the charged pair was found to be 0.69 ± 0.05. The G_H values at zero solute concentration calculated in model 3 ranged from 3.07 ± 0.05 to 3.18 ± 0.05 and were little affected by acid concentration.

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AQUEOUS SOLUTION; CHEMICAL RADIATION EFFECTS; CHEMICAL REACTION KINETICS; g VALUE; GAMMA RADIATION; HYDROGEN; HYDROGEN IONS; IRON IONS; IRON SULPHATES; OXYGEN; SOLVATED ELECTRONS; SULPHURIC ACID; WATER

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1. INTRODUCTION

The mechanism for the oxidation of ferrous ions by the species usually called 'H atom' has been the subject of numerous papers [Weiss 1950, Rigg *et al.* 1952, Allen & Rothschild 1957, Allen *et al.* 1957, Allen & Rothschild 1958, Czapski & Stein 1959, Stein 1960, Czapski *et al.* 1961, Boyle 1962, Katakis & Allen 1964]. There is no doubt that hydrogen ions are involved in the reaction, and authors of papers up to 1960 assumed a cationic form of H atom, H_2^+ or H_4O^+, existed and was the species reacting with ferrous species. Czapski *et al.* [1961] using atomic hydrogen produced in an electrodeless high frequency discharge, observed that a better fit to the data was provided by assuming that H atoms reacted directly with ferrous ions to form a hydride complex which subsequently decomposed to ferric ions and molecular hydrogen by reaction with hydrogen ions. Boyle [1962] favoured the H_4O^+ reaction with ferrous species but the suggestion of Czapski *et al.* [1961] has been widely accepted.

In a recent study of ^{60}Co gamma-irradiated ferrous sulphate/oxygen/0.4*M* sulphuric acid solutions [Matthews 1974], the results were interpreted in terms of reaction between H atom and ferrous species although there were indications of a possible contribution by an acid form of the H atom. That study also provided kinetic evidence for the existence of an excited water species. The following report deals with the extension of the study to solutions of other acid concentrations in order to obtain information on the effect of acid on the reaction of H atom in the acid form and also on the excited water yield.

It has been generally assumed that H atoms are the immediate product of reaction between hydrated electrons and hydrogen ions, but evidence has been presented that this is not so [Kongshaug *et al.* 1971, Cercek 1971] and the matter is the subject of argument [Neta *et al.* 1972, Kongshaug *et al.* 1972]. The present results are relevant to this argument.

2. EXPERIMENTAL

Materials, apparatus, and the experimental procedure were the same as previously described [Matthews 1974]. The dose rate was about 1 krad min^{-1}. Sodium sulphate decahydrate A.R. grade supplied by Merck was used without further purification. The molar extinction coefficient of ferric ion, $\varepsilon_{Fe^{3+}}$, in each different solution at 304 nm was determined relative to a value of 2180 M^{-1}cm^{-1} for ferric ion in 2 x 10^{-3}*M* ferrous sulphate/0.4*M* sulphuric acid solution [Matthews 1973].

Beer's law obtained, within instrumental error, for ferric ion solutions in 0.4*M* and 1.0*M* sulphuric acid; however, deviations from Beer's law beyond instrumental error were observed in 0.04*M* acid. The molar extinction coefficient of ferric ion was different at each acid concentration used and also depended to some extent on the ferrous sulphate concentration. The dependence on $\varepsilon_{Fe^{3+}}$ on the ferrous sulphate concentration was most marked at the lowest acid concentration. It was not appreciated in the previous study of 0.4*M* acid solutions [Matthews 1974] that $\varepsilon_{Fe^{3+}}$ increased by 1 per cent as the ferrous sulphate concentration increased from $1 \times 10^{-3}M$ to $50 \times 10^{-3}M$, therefore $G(Fe^{3+})$ values have been recalculated from these data and are reported here.

In 0.04*M* acid solutions a 7 per cent increase in $\varepsilon_{Fe^{3+}}$ resulted when the ferrous sulphate concentration was increased from $1 \times 10^{-3}M$ to $50 \times 10^{-3}M$. In order to moderate the variations in the forms of ferric and ferrous species present at different ferrous sulphate concentrations, solutions of 0.04*M* acid containing 0.1*M* sodium sulphate were used. In these solutions, the mean value of $\varepsilon_{Fe^{3+}}$ was approximately 2600 $M^{-1}cm^{-1}$ and independent of ferrous sulphate concentration. The molar extinction coefficients obtained for the various solutions are summarised in Figure 1. Deviations from Beer's law of up to 2 per cent were observed for ferric ions in 0.04*M* sulphuric acid/0.1*M* sodium sulphate solutions over the ferric ion concentration range used in the experiments. Consequently calibration curves were used for ferric ion concentrations in these solutions.

3. RESULTS

The reaction rate between hydrated electrons and ferric ions is reported to be 4×10^{10} ℓ $mol^{-1}s^{-1}$ [Czapski & Meisel 1971], which is one of the fastest rates known for reactions in aqueous solution. The reported reaction rate between hydrated electrons and hydrogen ions ($\sim 2 \times 10^{10}$ ℓ $mol^{-1}s^{-1}$) is also fast [Gordon *et al*. 1963a, 1963b, Dorfman & Taub 1963], so that in 0.4*M* and 1.0*M* sulphuric acid solutions at the ferric ion concentrations used, there was no significant reaction between hydrated electrons and ferric ions. In the 0.04*M* H_2SO_4/0.10*M* Na_2SO_4 system, however, approximately 1.5 per cent of the hydrated electron was calculated to react with ferric ion at the highest doses used (∿18 krad). Corrections were therefore applied to all the data from this system.

The measured ferric ion concentrations from the 1.0*M*, and 0.4*M* H_2SO_4 solutions and the corrected ferric ion concentrations from the 0.04*M* H_2SO_4/0.10*M* Na_2SO_4 solutions were directly proportional to absorbed radiation dose in the range 3 to 18 krad for all solutions except deoxygenated solutions containing less than 10 x $10^{-3}M$ ferrous ion concentration in the latter system. $G(Fe^{3+})_{obs}$ values were calculated from expression I and are given in Table 1.

$$G(Fe^{3+})_{obs} = \frac{\Delta[Fe^{3+}]\ min^{-1}\ (solution)}{\Delta[Fe^{3+}]\ min^{-1}\ (dosimeter)} \times 15.6$$

$$\times \frac{electron\ density\ \ (dosimeter)}{electron\ density\ \ (solution)} \quad . \qquad (I)$$

Where the relationship between ferric ion concentration and dose was linear, $\Delta[Fe^{3+}]\ min^{-1}$, the rate of change of ferric ion concentration, was obtained by the method of least squares. Where the relationship was non-linear, the initial $\Delta[Fe^{3+}]\ min^{-1}$ was obtained as discussed below.

The non-linearity was assumed to have been caused by competition between ferrous ions and ferric ions for H atoms (reactions 1 and 9*).

$$Fe^{2+} + H\cdot \overset{H^+}{\rightarrow} Fe^{3+} + H_2 \qquad (1)$$

$$Fe^{3+} + H\cdot \rightarrow Fe^{2+} + H^+ \quad . \qquad (9)$$

The concentration of ferric ion is plotted against dose for these solutions in Figure 2. The lines drawn through the points were calculated by numerical integration of expressions II and III.

$$\frac{d[Fe^{3+}]}{dt} = \Delta[Fe^{3+}]^{o} min^{-1} - 2\ \Delta[H]\ min^{-1}/(1 + k_1[Fe^{2+}]/k_9[Fe^{3+}]) \qquad (II)$$

$$\frac{d[Fe^{2+}]}{dt} = \frac{-d[Fe^{3+}]}{dt} \qquad (III)$$

where

the square parentheses denote molar concentrations,

$\Delta[Fe^{3+}]^{o}\ min^{-1}$ = the initial rate of formation of ferric ions, and

$\Delta[H]\ min^{-1}$ = the rate of formation of hydrogen atoms in the solution based upon an assumed value of 3.6 for G_H.

The best match of calculated line to the experimental points was found with a value of 0.6 for the ratio of rate constants (k_9/k_1). $G(Fe^{3+})_{obs}$ values corresponding to the initial rates of formation of ferric ions were calculated from expression I and are given in Table 1.

The ferric ion concentrations from deoxygenated solutions containing 0.4*M* and 1.0*M* sulphuric acid showed no significant curvature with doses up to

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* Equations identified in this paper by Arabic numbers correspond with those used in Matthews [1974].

18 krad for ferrous ion concentrations of $1 \times 10^{-3}M$ and greater. At extended doses, the 0.4*M* acid solutions gave curves consistent with a value of 0.08 for k_9/k_1; this was in agreement with the value found by Allen & Rothschild [1957]. $G(Fe^{3+})_{obs}$ values for deoxygenated solutions are plotted against the ferrous ion concentration in Figure 3.

4. DISCUSSION

At any given ferrous ion and sulphuric acid concentration the data are well described by the kinetic expression IV.

$$G(Fe^{3+})_{obs} = G^o + 2G_R/(1 + k_1[Fe]/k_2[O_2]) \qquad (IV)$$

where G^o = $G(Fe^{3+})$ at zero oxygen concentration,

= $2G_{H_2O_2} + G_{OH} + G_R$,

G_R = the number of radicals R per 100 eV which normally participate in reducing reactions, but which oxidise ferrous ions, (usually considered to be H atoms in acid solution),

k_1 and k_2 = the specific reaction rate constants for the reactions of R with ferrous species and oxygen, respectively, and

$[Fe]$ and $[O_2]$ = the concentrations of all forms of ferrous species and oxygen, respectively.

The parameters obtained from the data by the method of least squares, assuming the data to be described by expression IV, are given in Table 2; the G^o and G_R values are plotted against ferrous ion concentration in Figure 4.

The effect of acid concentration on yields of primary radiolytic species is reflected in the G^o and G_R values for the three systems; at any given ferrous ion concentration, G^o decreases with acid concentration and G_R is lowest at the lowest acid concentration. This effect has been recognised for many years and is thought to be associated with reactions of acid species with interspur species, but the details of the processes are not clearly established.

Several other features are readily distinguished. The G^o values at any given acid concentration, increase with increasing ferrous ion concentration whereas the G_R values appear to either decrease slightly or remain constant (0.4*M* sulphuric acid data). The k_1/k_2 value in each system, which ought to be a constant if the kinetic model is a good approximation of the true reaction mechanism, shows a pronounced decrease with increasing ferrous ion concentration.

The widely accepted model for irradiated water has, as the only significant primary radiolytic species diffusing into the bulk of the solution, hydrogen, hydrogen peroxide, hydrogen atoms, hydrated electrons, protons, hydroxyl radicals and, at high pH, the anion of hydroxyl radical, and combination and recombination reactions of radicals within the spur. In terms of this model the apparent decrease (or constancy, in the case of the 0.4*M* acid data) in G_R with a corresponding *increase* in G^o with increase in ferrous ion concentration, was unexpected. If, at higher concentrations,ferrous ions react within the spur with hydrogen atoms and hydroxyl radicals which would otherwise combine to give 'molecular products' hydrogen and hydrogen peroxide or recombine to give water, some increase in G_R would be expected with increase in ferrous ion concentration. This and other considerations [Matthews 1974] and the lack of constancy of the k_1/k_2 parameter led to the suggestion that the kinetic model described by expression IV was an over-simplification of the real system [Matthews 1974]. It was postulated that the increase in $G(Fe^{3+})_{deox}$ with increasing ferrous ion concentration in 0.4*M* acid solution arose from the presence of a significant yield of an excited water species among the primary radiolytic products and the reaction of ferrous ion with this species.

The $G(Fe^{3+})_{deox}$ values from the 1.0*M* acid and 0.04*M* acid/0.10*M* sodium sulphate (Figure 3) showed increases with ferrous ion concentration similar to the $G(Fe^{3+})_{deox}$ values from the 0.4*M* acid system. Therefore a similar involvement of excited water was assumed in these systems. In the consideration of various reactions between ferrous and excited water species, it was observed that the kinetic model providing the best fit to the data was based on a reaction between excited water and the ferrous bisulphate complex. The kinetic expression V was assumed to describe the data:

$$G(Fe^{3+})_{deox} = G^o_{(1,2,3)} + 2Gx_{(1,2,3)}/(1 + k_5/k_4[FeHSO_4^+]) \qquad (V)$$

where $G^o_{(1,2,3)}$ & $Gx_{(1,2,3)}$ indicate the G^o & Gx values in each of the three systems,

k_5 = the first or pseudo-first order decay constant of the excited water species, and

k_4 = the specific reaction rate constant for the reaction between the excited water species and the ferrous bisulphate complex.

The least squares method was used to obtain the seven parameters $G^o_{(1,2,3)}$ $Gx_{(1,2,3)}$ and k_5/k_4 and these are given in Table 3(a).

Since the values of $G_{x(1,2,3)}$ were constant within standard error a repeat analysis was made by the least squares method in which a single value for $G_{x(1,2,3)}$ was assumed in expression V. The five parameters evaluated are given in Table 3(b).

The reaction mechanism assumed for the kinetic analysis of all the data based on a single form of H atom and an independent yield of excited water, is given by reactions 1 to 5.

$$H\cdot + Fe^{2+} \rightarrow Fe\text{-}H^{2+} \qquad (1)$$

$$Fe\text{-}H^{2+} + H^{+} \rightarrow Fe^{3+} + H_2 \qquad (1a)$$

$$H\cdot + O_2 \rightarrow HO_2\cdot \ (\equiv 3Fe^{3+}) \qquad (2)$$

$$H_2O^* + O_2 \rightarrow H_2O_3 \text{ or } O_2\ (^1\Delta_g)\ (\equiv 4Fe^{3+}) \qquad (3)$$

$$H_2O^* + FeHSO_4^{+} \rightarrow FeSO_4^{+} + H\cdot + H_2O \qquad (4)$$

$$H_2O^* \rightarrow H_2O + \Delta \quad . \qquad (5)$$

The kinetic expression VI is derived from the above reaction sequence.

$$G(Fe^{3+}) = G^{o} + 2G_x\,(1 + 2k_3[O_2]/k_4[FeHSO_4^{+}])/A + 2(G_R + G_x/A)/(1 + k_1[Fe]/k_2[O_2]) \qquad (VI)$$

where

$$A = 1 + k_3[O_2]/k_4[FeHSO_4^{+}] + k_5/k_4[FeHSO_4^{+}] \quad .$$

Table 4 gives the ten parameters obtained by the least squares method and a form of expression VI in which individual values of G^{o} and G_R were assumed for the three systems, but single values of G_x and the ratios of rate constants. The parameters common to Tables 3 and 4 are seen to be in reasonable agreement.

The reaction sequence 1 to 5 is, therefore, a reasonable approximation of all the data,and supports the view that species additional to those already widely accepted and having the reaction characteristics of an excited water species, is an important primary product in irradiated acid solutions. Other evidence for excited water species comes from electron impact spectroscopy studies on water vapour [Compton *et al.* 1968, Knoop *et al.* 1972, Trajmar *et al.* 1973], on ice films [Lewis & Hamill 1969, Hunter *et al.* 1970], and from emission studies of gamma-irradiated ices from ordinary and heavy water [Bernas & Truong 1974].

4.1 Reaction Between Hydrated Electron and Ferrous Ion

The hydrated electron reacts with ferrous ion with a reported rate constant of about $2 \times 10^{8}\ \ell\ mol^{-1}s^{-1}$ [Baxendale *et al.* 1964, 1965] and with hydrogen ions with a reported rate constant of about 2×10^{10} ℓ $\text{mol}^{-1}\text{s}^{-1}$ [Gordon *et al.* 1963a, Dorfman & Taub 1963]. As there was a higher concentration of hydrogen ions than ferrous ions in all solutions but one, it was assumed that no significant reaction could occur between ferrous ions and hydrated electrons; however, to see if a better fit of the kinetic model to the low acid data could be obtained by assuming some reaction between ferrous ion and hydrated electron, the data were analysed with the assumption that $k(e^-_{aq} + Fe^{2+})$ had various values in the range 3×10^7 to 1.5×10^{10} ℓ $\text{mol}^{-1}\text{s}^{-1}$. No better fit could be obtained using any value for $k(e^-_{aq} + Fe^{2+})$ in this range. It was therefore concluded that there was no significant reaction between hydrated electron and ferrous ion in the solutions studied.

4.2 Reversibility of Hydrogen Atom with Ferrous Ion Reaction

Czapski *et al.* [1961] have postulated that reaction 1 is reversible. The kinetic expression VII is derived from reactions 1 to 5 when reaction 1 is rewritten as the reversible reaction below:

$$H\cdot + Fe^{2+} \underset{-1}{\overset{1}{\rightleftarrows}} Fe\text{-}H^{2+} \quad . \qquad (1)$$

$$\begin{aligned} G(Fe^{3+}) = G^{o} &+ 2G_x(1 + 2k_3[O_2]/k_4[FeHSO_4^+])/A \\ &+ 2(G_R + G_x/A)\ (1 + k_{-1}/k_{1a}[H^+])/ \\ &\quad (1 + k_1[Fe]/k_2[O_2] + k_{-1}/k_{1a}[H^+]) \quad . \end{aligned} \qquad (VII)$$

None of the data were fitted satisfactorily to expression VII by the least squares method, therefore no significant dissociation of the ferric hydride complex was observed in the present experimental results.

4.3 Two Forms of H Atom

One of the implicit assumptions of the preceding treatment of the data is that hydrated electrons react rapidly with hydrogen ions to give H atoms which are identical to those formed in any other radiolytic process. The G_R evaluated is, therefore, $G_{e^-_{aq}} + G_H$. It was of interest to evaluate the data in terms of the reactions proposed by Katakis & Allen [1964], involving an acid form of the H atom, H_2^+, since this species was at one time widely thought to be involved in the reaction. In addition to reactions 1 and 2 they assumed the reactions

$$H\cdot + H^+ \rightarrow H_2{}^+ \qquad (6)$$

$$H_2^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2 \quad . \qquad (7)$$

Taken together with reactions 1 to 5, these reactions lead to the kinetic expression:

$$G(Fe^{3+}) = G^{o} + 2G_X\ (1 + 2\ k_3[O_2]/k_4[FeHSO_4^+])/A$$
$$+ 2(G_R + G_X/A)/(1 + k_1[Fe]/k_2[O_2]$$
$$+ k_6[H^+]/k_2[O_2]) \quad . \qquad (VIII)$$

The data from each of the three acid solutions were assumed to be described by expression VI in one analysis and by expression VIII in another; the parameters so obtained are given in Tables 5(a) and 5(b). Expression VIII gave a significantly better fit to the data than expression VI for the two least acid solutions, suggesting reactions of more than one form of H atom in these solutions.

The parameter $k_6[H^+]/k_2$ decreases with increasing acidity (Table 5). Since there is no obvious reason why reaction 2, the reaction of H atoms with neutral oxygen molecules, should be affected by change in acid concentration, the parameter $k_6[H^+]/k_2$ ought to increase with increase in hydrogen ion concentration if the model is correct. It is concluded, therefore, that the reaction sequence 1 to 7 is incorrect.

It should be noted, however, that if it is assumed that H atoms are predominantly in an acid form, say H_2^+, at the hydrogen ion concentrations of these solutions, as was concluded by Allen & Rothschild [1958], the 'H' of reactions 1 and 2 becomes H_2^+, the second form of H atom may be that formed in the reverse of reaction 6, and reaction 7 may be replaced by reaction 1. The fit of the expression derived from this mechanism to the data is identical to that given in Table 5(b). The parameters have the same numerical value. The ratio k_1/k_2 becomes the rate ratio for reaction of H_2^+ radicals with ferrous ions and oxygen and the parameter $k_6[H^+]/k_2$ becomes k_{-6}/k_2. In order to explain the decrease in k_{-6}/k_2 with increasing hydrogen ion concentration, a reversibility of reaction -6 may be assumed. The rearranged reaction sequence is given below:

$$H_2^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2 \qquad (11)$$
$$H_2^+ + O_2 \rightarrow HO_2 + H^+ \qquad (12)$$
$$H_2^+ \rightleftarrows H\cdot + H^+ \quad . \qquad (-6)$$

Expression VIII takes no account of reactions of the minor component of the H atom with oxygen. It is assumed that the reaction between H atoms formed in reaction -6 and oxygen is fast and should be included in any complete reaction scheme describing the irradiated ferrous sulphate/oxygen system. Since the model now under consideration assumes H_2^+ to be the predominant form of the H atom species it is further assumed that reaction 4 also gives H_2^+ by some fast process. The following kinetic expression is therefore derived from the reactions 1 to 6, -6, 11, 12.

$$\begin{aligned} G(Fe^{3+}) = {} & G^o + 2G_x(1 + 2k_3[O_2]/k_4[FeHSO_4^+])/A \\ & + 2(G_R + G_x/A)\ (1 + k_{-6}k_2/(k_{12}k_1[Fe]B))/ \\ & (1 + k_{11}[Fe]/k_{12}[O_2] + k_{-6}(1 + k_2[O_2]/k_1[Fe])/ \\ & (k_{12}[O_2]B)) \qquad \text{(IX)} \end{aligned}$$

where $B = 1 + k_2[O_2]/k_1[Fe] + k_6[H^+]/k_1[Fe]$.

In an attempt to decrease the number of adjustable parameters in expression IX, use was made of the material balance relationship

$$2G_{H_2} + G_H = 2G_{H_2O_2} + G_{OH} \quad .$$

Since $G^o = 2G_{H_2O_2} + G_{OH} + G_H$,

$2(G_{H_2} + G_H)$ may be substituted for G^o and, by a further substitution of numerical values for G_{H_2}, the three parameters for G^o are eliminated. The numerical values of 0.42, 0.40 and 0.39 obtained from the data of Sehested *et al.* [1973] were used for three solutions. The hydrogen ion concentrations in the 1.0 and 0.4*M* sulphuric acid solutions were estimated from the data of Young *et al.* [1959], and, in the 0.04*M* acid/0.1*M* sodium sulphate solutions, from the data of Baes [1957].

The parameters obtained by applying the least squares method to the combined data and using the material balance substitution in expression IX are given in Table 6.

The overall fit to the combined data as shown by the variance is better than that shown in Table 4 using a single form of H atom and expression VI. However, the parameters common to both Table 6 and those evaluated from the deaerated data alone in Table 3 are not in good agreement and the standard errors for the fine structure kinetic parameters are quite large. The improved fit may therefore be a fortuitous consequence of the additional adjustable parameters provided by expression IX.

4.4 Kinetic Salt Effect

Another factor which relates to the possibility of two forms of H atom in the oxidation of ferrous ion is the kinetic salt effect. The reaction mechanism postulated involved a competition between solutes, one of which is charged (Fe^{2+}) and the other uncharged (O_2) for reactions with two forms of H atom, one of which is charged.

The kinetic salt relationship is given by the expression [Czapski & Schwarz 1962]:

$$\log_{10} \frac{k}{k_o} = 1.02\ ZaZb \frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (X)$$

where k, k_o = the rate constants at ionic strength, μ, and zero respectively,

ZaZb = the algebraic product of charges on the reactive species a and b.

The values of $\log_{10} k_{11}/k_{12}$ obtained from Table 6 are plotted against the appropriate values of $\sqrt{\mu}/(1 + \sqrt{\mu})$ in Figure 5. The ionic strength of the solutions was calculated from the data of Young *et al.* [1959] and Baes [1957]. It is seen that a reasonably straight line with a positive slope of about 0.5 can be drawn through the plotted points. According to expression X, a positive slope is to be expected for reaction between species of like charge.

If the species whose reaction rate ratio is given by k_{11}/k_{12} is entirely H_2^+, and if all the ferrous species are present as a single species of doubly charged hydrated Fe^{2+} ions, then for ideal behaviour a slope of 2.04 is predicted. However, the ferrous species are not all present as one species of doubly charged ions. There is evidence that ferrous ions form weak complexes with bisulphate and sulphate ions with association constants of 0.4 and 2.0 respectively at a solution ionic strength of 1.0 [Jayson *et al.* 1972]. Applying the Debye-Huckel corrections for ionic strength, apparent association constants for the complexes at the ionic strengths of the three acid solutions may be calculated, and by combining these with the data for the bisulphate and sulphate ion concentrations [Young *et al.* 1959, Baes 1957], the proportion of each ferrous species present may then be calculated. The result of this calculation is shown in Table 7. The result also shows that the mean charge on ferrous species present in each acid solution is approximately 1.4. Therefore for ideal kinetic salt behaviour, and assuming that each species reacts with H_2^+ at the same rate, we expect a slope of about 1.4 not 2.04.

It has been observed by Perlmutter-Hayman [1972] that, for reactions between ions of unlike sign, classical salt-effect behaviour obtains, but for reactions between ions of like sign, the principle of ionic strength seems to break down completely. The rate in this case is determined by the concentration of the supporting ion of opposite charge.

The failure of the k_{11}/k_{12} parameters in Table 6 to give the theoretical kinetic salt relationship is, therefore, not conclusive evidence against an

$H_2^+ + Fe^{2+}$ reaction but neither is the qualitative agreement with the relationship strong evidence in support of the reaction.

The possibility of the H atom existing as H_2^+ was maintained by Allen & Rothschild [1958]. In their view the H atom existed predominantly in the acid form up to as high as pH 2.1. Subsequently, Katakis & Allen [1964] repudiated this viewpoint on the basis of their failure to observe any significant change in the rate constants of ferrous oxidation by the H atom species when the sulphuric acid concentration was varied over the range 0.2*M* to 2.2*M*. However it does not appear that their data convincingly rule out the possibility that the H atom is already predominantly in the form of H_2^+ at acid concentrations lower than 0.2*M* sulphuric acid.

4.5 Possibility of H_3O

It has been generally accepted that H atoms are the product of reaction between hydrogen ions and hydrated electrons, the major primary reducing species present in irradiated water [Neta *et al.* 1972]. The reaction is almost diffusion controlled and, therefore, it has also been generally assumed that H atoms are the major primary-reducing species present in acid solutions. Evidence has been given that the situation might not be as simple as this; it is claimed that H atoms are not the immediate product of reaction between hydrogen ions and hydrated electrons but a hydrated H atom species, designated as H_3O, which decays to H atoms in a first order process of rate constant $\sim 10^5 s^{-1}$ [Kongshaug *et al.* 1971, Cercek 1971].

Probably the most persuasive evidence against H_2^+ reaction with ferrous ion in irradiated acidified aqueous solutions comes from the results of Czapski *et al.* [1961], provided that it is assumed that H atoms are the immediate reaction product from collisions between hydrated electrons and hydrogen ions. In that study H atoms were generated by electrodeless discharge and used to oxidise ferrous ions. If H atoms are not the immediate product of reaction between hydrated electrons and hydrogen ions as is claimed by Kongshaug *et al.* [1971] and Cercek [1971], the results of Czapski *et al.* [1961] are not applicable to irradiated aqueous solutions except for the small amount of H atoms, formed by decay of H_3O, which escape reaction with solutes and H atoms formed by processes other than *via* hydrated electrons.

If the claims of Kongshaug *et al.* [1971] and Cercek [1971] are correct the reactions 11, 12, and -6 could involve H_3O in place of H_2^+ and be rewritten

$$H_3O + Fe^{2+} \rightarrow Fe\text{-}H^{2+} + H_2 \tag{21}$$

$$H_3O + O_2 \rightarrow HO_2 + H_2O \tag{22}$$

$$H_3O \rightarrow H\cdot + H_2O \quad . \tag{-26}$$

The kinetic expression derived from reactions 21, 22, 3, 4, 5, -26, and 1 has the same form as expression VIII and provides an excellent fit to the data from the three separate acid systems. It does not, however, account for the observed dependence of the rate of first order decay to H atoms on the hydrogen ion concentration; hence it is necessary to invoke an acid form of H_3O together with a reversibility of the reaction equivalent to -26. This leads to the following reaction sequence:

$$e^-_{aq} + H_3O^+ \rightarrow H_3O \tag{20}$$

$$H_3O + H_3O^+ \rightarrow H_4O^+ + H_2O \tag{30}$$

$$H_4O^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O + H_2 \tag{31}$$

$$H_4O^+ + O_2 \rightarrow HO_2 + H_3O^+ \tag{32}$$

$$H_4O^+ \rightleftarrows H\cdot + H_3O^+ \quad . \tag{-36}$$

Reactions 31, 32, and -36 are equivalent to reactions 11, 12, and -6, the only difference being a water molecule associated with the H_2^+ species as suggested by Weiss [1950]. The kinetic expression describing the sequence together with reactions 1 to 5 has the same form as expression IX.

4.6 Summary of Results from Excited Water Model

The results of the analyses based on reactions invoking an independent yield of an excited water species in addition to the usual primary radiolytic species provide some evidence for the existence of the H atom in more than one form. However, the fact that some of the parameters evaluated in the analyses have large standard errors and that there is not perfect agreement between parameters evaluated from all the data and the deaerated data only, leads to the suspicion that the improved fit of the model involving two forms of H atom may be fortuitous. Considerations of the kinetic salt relationship, although in qualitative agreement with a significant reaction between positively charged ferrous species and a positively charged form of H atom, gave no conclusive result.

4.7 Diffusion Kinetic Model

An alternative explanation to the excited water postulate for the increase in $G(Fe^{3+})_{deox}$ with ferrous ion concentration is that there is no reaction of ferrous species with excited water but that ferrous ion is inhibiting water reformation reactions within the spur. In view of the moderate reaction rates of ferrous species with primary radiolytic species [Anbar & Neta 1967], the reason for the efficiency of this process is not clear but, for the present evaluation, it will be assumed to be the sole process responsible for the $G(Fe^{3+})_{deox}$ results. The well established empirical cube root relationship will be assumed to describe the results. The data obtained from deoxygenated solutions are, therefore, given by the expression:

$$G(Fe^{3+})_{deox} = G^{o}(1,2,3) + C[Fe]^{1/3} \qquad (XI)$$

where C = the cube root coefficient.

Application of the least squares method and expression XI to the data gave the parameters listed in Table 8(a).

It will also be assumed that, since the reaction rate for H atom species with oxygen appears to be two to three orders of magnitude faster than with ferrous species, oxygen will dominate spur reactions involving H atom species. G_R will therefore be assumed to increase by $D[O_2]^{1/3}$ at any given oxygen concentration. The kinetic expression XII is derived by assuming the above cube root increase in yields, a single form of H atom, and the material balance relationship:

$$G(Fe^{3+}) = 2(G_{H_2} + G_{R_{1,2,3}}) + C[Fe]^{1/3} + D[O_2]^{1/3}$$
$$+ 2(G_{R_{1,2,3}} + D[O_2]^{1/3})/(1 + k_1[Fe]/k_2[O_2]) \qquad (XII)$$

where G_{H_2} was assigned the numerical values of 0.42, 0.40 and 0.39 for the 0.04*M* H_2SO_4/0.10*M* Na_2SO_4, 0.40*M* H_2SO_4, and 1.0*M* Na_2SO_4 solutions respectively.

The parameters evaluated by the least squares method, assuming expression XII, are given in Table 8(b).

The variances of fit given for the analyses in Tables 8(a) and 8(b) are fairly high and the fits to the data by the expressions XI and XII are comparatively poor. It is also noted that the values obtained for the cube root coefficient C are not in good agreement in either analysis. No significantly better fit was obtained using other modifications of the cube root expression when only a single form of H atom was assumed.

A repeat analysis was made assuming that two forms of H atoms are involved and that the reaction mechanism is given by reactions 31, 32, -36, 1, 2, and 36. The kinetic expression XIII is derived for this mechanism:

$$G(Fe^{3+}) = 2(G_{H_2} + G_{R_{1,2,3}}) + C[Fe]^{1/3} + D[O_2]^{1/3}$$
$$+ 2(G_{R_{1,2,3}} + D[O_2]^{1/3})\ (1 + k_{-36}\, k_2/(k_{32}\ k_1[Fe]B))/$$
$$(1 + k_{31}[Fe]/k_{32}[O_2] + k_{-36}\ (1 + k_2[O_2]/k_1[Fe])/$$
$$(k_{32}[O_2]B)) \quad . \qquad (XIII)$$

The parameters obtained from the combined data using expression XIII and the least squares method are given in Table 9.

A considerable improvement in the fit to the data is achieved using expression XIII; however, the standard errors in the kinetic parameters k_{-36}/k_{32}, k_{36}/k_1, and k_2/k_1 are once again quite large, and the disagreement between the cube root coefficient C of Table 8(a) and Table 9 is even worse. There is no evidence for any kinetic salt effect on the parameter k_{31}/k_{32}.

4.8 Charge Pair Recombination Model

An alternative possibility to the postulate of an independent yield of an excited water species or the cube root model is the inhibition of recombination of the charge pair, $H_2O^+...e^-$, by sulphuric acid species together with oxidation of ferrous ion. The stoichiometry is assumed to be given by reaction 13:

$$H_2O^{+}..e^- + HSO_4^- + Fe^{2+} \rightarrow FeSO_4^+ + H_2O + H\cdot \quad . \qquad (13)$$

The solute concentration dependence of product yield in irradiated cyclohexane solution has been shown by Infelta & Schuler [1972] to be well described by expressions containing the term $G_{gi}\ \sqrt{\alpha[S]}\ /\ (1 + \sqrt{\alpha[S]})$, where G_{gi} is the 100 eV yield of geminate ion pair, α is a reactivity constant for the solute S, and the square brackets denote concentrations. Expressions involving this term have been found to provide a very good approximation to data from non-aqueous (listed in Infelta 1972) and aqueous [Balkas & Schuler *et al.* 1970] systems.

The kinetic expression for reaction 13 in competition with recombination of the charge pair is therefore given by expression XIV:

$$G(Fe^{3+}) = G^{o}_{1,2,3} + 2G_{cp}/(1 + 1/\sqrt{\alpha[HSO_4^-]\ [Fe^{2+}]}) \qquad (XIV)$$

where G_{cp} = the 100 eV yield of the charged pair

α = the reactivity constant for reaction 13.

Expression XIV was fitted to the data by the least squares method. The following parameters were obtained:

$G^{o}_{1,2,3}$ = 7.03 ± 0.06, 7.26 ± 0.07, 7.22 ± 0.07

G_{cp} = 0.70 ± 0.03

$$\alpha = (8.3 \pm 2.6) \times 10^2 M^{-2}.$$

The variance of fit was 2.54×10^{-3}. The lines calculated by substituting these parameters in expression XIV are shown together with the experimental points in Figure 3.

The following equations, analogous to equation 13, are obtained by assuming involvement of the other sulphuric acid species, sulphate ions and hydrogen ions:

$$H_2O^+ \ldots e^- + SO_4^= + Fe^{2+} \rightarrow FeSO_4^+ + OH^- + H\cdot \qquad (14)$$

$$H_2O^+ \ldots e^- + H^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O + H\cdot \quad . \qquad (15)$$

The sulphate anion does not appear to be implicated since high concentration of sodium sulphate has no effect on product yields [Allen *et al.* 1957, Fisher & Hamill 1973]. The parameters obtained by the least squares method when the hydrogen ion concentration was substituted in expression XIV in place of the bisulphate ion concentration, were

$$G^o_{1,2,3} = 7.07 \pm 0.05,\ 7.16 \pm 0.06,\ 7.11 \pm 0.07$$

$$G_{cp} = 0.73 \pm 0.03$$

$$\alpha = (6.86 \pm 1.8) \times 10^2 \ .$$

The variance of fit was 2.60×10^{-3}. The fact that $G^o_{1,2,3}$ were in agreement within standard error in this analysis suggested a further analysis in which a single value of G^o was assumed in expression XIV (hydrogen ion form). The parameters obtained in the repeat analysis were

$$G^o = 7.04 \pm 0.06$$

$$G_{cp} = 0.77 \pm 0.03$$

$$\alpha = (8.11 \pm 2.2) \times 10^2 \ .$$

The variance of fit was 3.3×10^{-3}.

Therefore, the assumption that the increase in $G(Fe^{3+})_{deaer}$ with ferrous ion concentration at various sulphuric acid concentrations is due to reaction 15 leads to a common value of 7.04 ± 0.06 for $2G_{H_2O_2} + G_R + G_{OH}$ which is independent of sulphuric acid concentration at zero ferrous ion concentration. If reaction 13 is assumed, then a slight increase in G^o with increasing sulphuric acid concentration 7.03 ±0.06 to 7.22 ± 0.07 is obtained. The G^o values from both analyses are significantly lower than the $2G_{H_2O_2} + G_R + G_{OH}$ values given in standard text books for primary radiolytic yields at these acid concentrations [Draganic & Draganic 1971] and are more in agreement with the sum of the values obtaining in neutral solutions. Also contrary to the text books is the absence of a marked increase in the primary radiolytic yields with increasing acid concentration.

The results of the least squares analysis, using expression XIV, show that if the reaction

$$H_2O^+ \ldots e^- + HSO_4^- \rightarrow .SO_4^- + H\cdot + H_2O \qquad (16)$$

occurs, it makes only a small contribution to the net effect. The possibility of reaction 16 followed by ferrous ion oxidation in competition with bisulphate ion reformation was also considered. However, no support for this mechanism was obtained because expression XV

$$G(Fe^{3+}) = G^o_{1,2,3} + 2G_{cp}/(1 + 1/\sqrt{\alpha[HSO_4^-]})/(1 + 1/\sqrt{\gamma[Fe^{2+}]}) \qquad (XV)$$

gave a poor fit to the data.

The results of the analyses of the deaerated data on the basis of a charge pair recombination model therefore support the view that charge pair oxidation of the ferrous ion is facilitated by either hydrogen ions or bisulphate ions, and that the apparent increase in primary radiolytic yields with increasing acid concentration is due to a contribution to the product yield from this reaction. Since the charge pair recombination model provides a good fit to the deaerated data, the possible additional reactions occurring in the presence of oxygen were considered. It is assumed that in the presence of oxygen the reaction

$$H_2O^+ \ldots e^- + HSO_4^- + O_2 \rightarrow HO_2\cdot + .SO_4^- + H_2O \qquad (17)$$

occurs in competition with reaction 13.

The following kinetic expression therefore should describe the data:

$$G(Fe^{3+}) = G^o_{1,2,3} + \frac{2G_{cp} \cdot \dfrac{\alpha[Fe]}{\alpha[Fe] + \beta[O_2]}}{(1 + 1/\sqrt{[HSO_4^-](\alpha[Fe]+\beta[O_2])})} + \frac{4G_{cp} \cdot \dfrac{\beta[O_2]}{\alpha[Fe] + \beta[O_2]}}{(1 + 1/\sqrt{[HSO_4^-](\alpha[Fe]+\beta[O_2])})}$$

$$+ 2\left\{\frac{G_R + \dfrac{G_{cp} \cdot \dfrac{\alpha[Fe]}{\alpha[Fe] + \beta[O_2]}}{(1 + 1/\sqrt{[HSO_4^-](\alpha[Fe]+\beta[O_2])})}}{1 + \dfrac{k_1[Fe]}{k_2[O_2]}}\right\} \quad . \qquad (XVI)$$

Substitution of the material balance relationship for G^o in expression XVI and application of the least squares method gave the results in Table 10. It is seen that the G_{cp} and α parameters are in agreement, within standard error, with those obtained from the deaerated data using expression XIV. It is also observed that G_{R_2} and G_{R_3} have essentially the same value, and therefore it follows that the entire data could be fitted equally well with a form of expression XIV involving only six adjustable parameters. The overall fit to the data is probably quite reasonable considering the uncertainties inherent in the oxygen concentration of the solutions. The calculated values for $G(Fe^{3+})$ from expression XIV and the parameters in Table 10 are compared with the experimental values in Table 1.

The possibility of reaction of two forms of H atom according to reactions 31, 32, -36, 1, 2 and 36, together with bisulphate ion inhibition of the charge pair recombination was also considered. The kinetic expression describing the data and incorporating the material balance relationship would in this case be

$$G(Fe^{3+}) = 2(G_{H_2} + G_{R_{1,2,3}}) + 2G_{cp}\,\frac{(\alpha[Fe] + 2\beta[O_2])/(\alpha[Fe] + \beta[O_2])}{(1 + 1/\sqrt{([HSO_4^-](\alpha[Fe] + \beta[O_2]))})}$$

$$+ \frac{2(G_{R_{1,2,3}} + \dfrac{G_{cp}\,\alpha[Fe]/(\alpha[Fe] + \beta[O_2])}{(1 + 1/\sqrt{([HSO_4^-](\alpha[Fe] + \beta[O_2]))})})\ (1 + \dfrac{k_{-36}}{k_{32}} \cdot \dfrac{k_2}{k_1[Fe]B})}{1 + \dfrac{k_{31}[Fe]}{k_{32}[O_2]} + \dfrac{k_{-36}}{k_{12}[O_2]}\ \dfrac{(1 + \dfrac{k_2[O_2]}{k_1[Fe]}}{B}} \qquad (XVII)$$

where $B = 1 + \dfrac{k_2[O_2]}{k_1[Fe]} + \dfrac{k_{36}[H^+]}{k_1[Fe]}$.

The data were treated by the least squares method assuming expression XVII but convergence was not achieved. This result supports the view that the improved fit obtained using the two forms of H atom model with both the previous treatments was probably fortuitous and leads to the conclusion that there is no real evidence in the present data for significant reaction of two forms of H atom.

There are a number of theories for radiolytic processes occurring in concentrated aqueous solutions. An excellent summary of these has been given by Wolff *et al.* [1975]. Their results show that an initial yield of 4.8 electrons per 100 eV is formed which can react with solutes at sufficiently high concentration in competition with recombination processes with the reactive species in the radiation spur. Their results are consistent with the model proposed by Hamill [1969], Bevan & Hamill [1970] and Sawai & Hamill [1970] that e^- and H_2O^+, the two initial products of the original ionisation event, known as the 'dry' electron and 'dry' hole, can take part in reactions or recombine in the spur. Other data on concentrated solutions obtained by Aldrich *et al.* [1975] indicate that the hydrogen ion does not react with the charge pair and, therefore, the correlation obtained in this work with the hydrogen ion concentration is probably only the consequence of the similarity of hydrogen ion and bisulphate ion concentrations in these solutions.

The interpretation of the present results in terms of participation by the charge pair species does not distinguish the details of these early primary radiolytic processes but the consistency of the parameters and the agreement between calculated and experimental yields over the entire acid and solute concentration range indicate that the proposed reactions are a good approximation to the reaction stoichiometry. The results also indicate the importance of reactions of charge pair species in irradiated sulphuric acid solutions. It seems likely that reactions of charge pair species will be of importance in most aqueous solutions containing high concentrations of solutes.

4.9 Total Ionisation Yields

There appears to be general agreement between workers concerned with primary yields of radiolytic species in concentrated solution that the initial yield of electrons is 4.8 or higher per 100 eV [Schwarz 1969, Balkas *et al.* 1970, Freeman 1968, Hamill 1969, Koulkes-Pujo *et al.* 1971]. The present results are consistent with a total ionisation yield of 4.7 ± 0.15 for the 1.0*M* and 0.4*M* sulphuric acid solutions and 4.6 ± 0.15 for the 0.04*M*/0.10*M* sodium sulphate solutions respectively. These estimates are obtained from the summation

$$2G_{H_2} + G_R + G_{cp} \quad .$$

4.10 Primary Radiolytic Yields

It has already been noted that the G^o values obtained using the charge pair model for the deaerated data are significantly lower than the values given in the standard texts for these solutions [Matthews 1976]. Since G^o is equal to $2G_{H_2O_2} + G_H + G_{OH}$, it was inferred that the primary radiolytic yields estimated in acid solutions for zero scavenger concentration are erroneously high. The present results from solutions at all oxygen concentrations confirm that the reducing radical yield is little affected by increasing acid concentration, the values being in reasonable agreement with published values for $G_{e^-_{aq}} + G_H$ in neutral solution. It is suggested that published estimates for $G_{e^-_{aq}} + G_H$ in acid solutions generally contain a significant contribution from reactions of charge pair species which have not been taken into account.

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TABLE 1

$G(Fe^{3+})$ VALUES FOR FERROUS SULPHATE SOLUTIONS AT VARIOUS SOLUTE AND ACID CONCENTRATIONS

1*M* H_2SO_4				0.4*M* H_2SO_4				0.04*M* H_2SO_4/0.1*M* Na_2SO_4			
$[Fe^{2+}]$ *M*x10^3	$[O_2]$ *M*x10^6	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ *M*x10^3	$[O_2]$ *M*x10^6	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ *M*x10^3	$[O_2]$ *M*x10^6	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)
1.0	0	7.78	7.83	0.2	5.8	14.55	14.44	1.0	0	7.24	7.27
1.0	0	7.81	7.83	0.2	15.3	15.04	14.88	1.0	0	7.25	7.27
1.0	0	7.83	7.83	0.2	16.1	15.09	14.91	1.0	6.2	12.70	12.90
1.0	4.41	13.68	13.70	0.2	86.0	15.12	15.49	1.0	17.5	13.86	13.70
1.0	11.7	14.92	14.69	0.2	230	15.41	15.74	1.0	96.5	14.75	14.51
1.0	71.6	15.57	15.59	0.2	1095	15.91	16.00	1.0	261	15.00	14.88
1.0	202	15.76	15.85	0.2	1095	15.98	16.00	1.0	1262	15.19	15.33
1.0	966	16.13	16.07	1.0	0	7.69	7.70				
1.0	966	16.13	16.07	1.0	0	7.71	7.70				
2.0	0	7.92	7.95	1.0	5.5	13.61	13.69	2.0	0	7.33	7.35
2.0	0	7.95	7.95	1.0	15.3	14.87	14.60	2.0	0	7.35	7.35
2.0	4.62	12.58	12.94	1.0	86.0	15.21	15.44	2.0	6.2	11.79	12.26
2.0	11.6	14.50	14.25	1.0	230	15.55	15.72	2.0	17.5	13.65	13.42
2.0	71.6	15.46	15.51	1.0	1095	15.75	16.00	2.0	95.7	14.62	14.46
2.0	200	15.68	15.82	2.0	0	7.86	7.81	2.0	261	14.81	14.86
2.0	975	16.20	16.06	2.0	0	7.88	7.81	2.0	1262	15.14	15.33
2.0	975	16.15	16.06	2.0	5.5	12.85	12.97				
5.0	0	8.11	8.10	2.0	15.3	14.34	14.26				
5.0	0	8.18	8.10	2.0	86.0	15.18	15.37				
5.0	4.4	11.01	11.40	2.0	86.0	15.20	15.37				

TABLE 1 (Cont.)

$1M\ H_2SO_4$				$0.4M\ H_2SO_4$				$0.4M\ H_2SO_4/0.1M\ Na_2SO_4$			
$[Fe^{2+}]$ $M\times10^3$	$[O_2]$ $M\times10^6$	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ $M\times10^3$	$[O_2]$ $M\times10^6$	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ $M\times10^3$	$[O_2]$ $M\times10^6$	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)
5.0	12.4	13.45	13.30	2.0	230	15.60	15.69				
5.0	71.6	15.28	15.26	2.0	1095	15.87	16.00				
5.0	195	15.69	15.71	2.0	1100	16.08	16.00				
5.0	1008	16.10	16.05								
5.0	1008	16.04	16.05								
10.0	0	8.26	8.19	10.0	0	7.97	8.08	10.0	0	7.61	7.60
10.0	0	8.15	8.19	10.0	0	8.20	8.08	10.0	0	7.59	7.60
10.0	4.41	10.13	10.33	10.0	5.5	10.49	10.53	10.0	6.5	10.06	10.12
10.0	12.4	12.23	12.19	10.0	15.3	12.28	12.40	10.0	17.4	12.03	11.83
10.0	70.4	14.74	14.84	10.0	86.0	14.76	14.84	10.0	95.7	14.16	14.03
10.0	195	15.47	15.55	10.0	230	15.32	15.48	10.0	265	14.70	14.70
10.0	1008	16.10	16.01	10.0	1095	15.86	15.95	10.0	1262	15.22	15.28
10.0	1008	16.11	16.01								
20.0	0	8.31	8.27					20.0	0	7.66	7.72
20.0	0	8.37	8.27	20.0	0	8.17	8.18	20.0	0	7.69	7.72
20.0	4.34	9.55	9.51	20.0	5.5	9.70	9.66	20.0	6.6	9.29	9.30
20.0	12.4	11.07	11.00	20.0	15.3	11.33	11.25	20.0	17.4	10.92	10.79
20.0	74.1	14.25	14.20	20.0	86.0	14.22	14.25	20.0	95.7	13.63	13.55
20.0	197	15.21	15.24	20.0	230	15.39	15.22	20.0	265	14.53	14.50
20.0	1000	15.99	15.94	20.0	1095	16.19	15.88	20.0	1262	15.15	15.24
50.0	0	8.36	8.35	50.0	0	8.40	8.29	50.0	0	7.76	7.87

TABLE 1 (Cont.)

1M H_2SO_4				0.4M H_2SO_4				0.4M H_2SO_4/0.1M Na_2SO_4			
$[Fe^{2+}]$ $M\text{x}10^3$	$[O_2]$ $M\text{x}10^6$	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ $M\text{x}10^3$	$[O_2]$ $M\text{x}10^6$	$G(Fe^{2+})$ (obs)	$G(Fe^{3+})$ (calc)	$[Fe^{2+}]$ $M\text{x}10^3$	$[O_2]$ $M\text{x}10^6$	$G(Fe^{3+})$ (obs)	$G(Fe^{3+})$ (calc)
50.0	0	8.36	8.35	50.0	0	8.33	8.29	50.0	0	7.84	7.87
50.0	4.34	8.95	8.91	50.0	5.5	9.02	8.97	50.0	6.6	8.42	8.62
50.0	12.4	9.81	9.75	50.0	15.3	10.06	9.93	50.0	17.4	9.68	9.57
50.0	74.8	12.72	12.79	50.0	86.0	13.10	12.95	50.0	95.8	12.54	12.45
50.0	197	14.14	14.41	50.0	230	14.98	14.50	50.0	265	13.99	13.93
50.0	995	15.82	15.74	50.0	532	15.32	15.31	50.0	1273	14.97	15.10
50.0	995	15.71	15.74	50.0	1095	15.85	15.71				
				50.0	1095	16.03	15.71				
				100.0	0	8.43	8.35				

TABLE 2

LEAST SQUARES ANALYSES OF INDIVIDUAL DATA SETS USING EXPRESSION IV

	$[Fe^{2+}]$ *M* x 10^3	G^o	G_R	k_1/k_2 x 10^3	Variance
	1.0	7.25 ± 0.08	3.91 ± 0.05	2.83 ± 0.20	1.25 x 10^{-2}
	2.0	7.35 ± 0.09	3.85 ± 0.06	2.18 ± 0.15	1.50 x 10^{-2}
0.04*M* H_2SO_4/	10.0	7.60 ± 0.08	3.78 ± 0.06	1.30 ± 0.08	1.37 x 10^{-2}
0.10*M* Na_2SO_4	20.0	7.68 ± 0.05	3.76 ± 0.04	1.20 ± 0.05	5.18 x 10^{-3}
	50.0	7.68 ± 0.06	3.75 ± 0.05	1.09 ± 0.07	9.9 x 10^{-3}
	1.0	7.70 ± 0.11	3.95 ± 0.07	1.82 ± 0.20	2.26 x 10^{-2}
	2.0	7.87 ± 0.16	3.94 ± 0.09	1.67 ± 0.20	4.91 x 10^{-2}
0.4*M* H_2SO_4	10.0	8.10 ± 0.09	3.86 ± 0.06	1.28 ± 0.08	1.53 x 10^{-2}
	20.0	8.24 ± 0.14	4.00 ± 0.08	1.29 ± 0.12	2.35 x 10^{-2}
	50.0	8.35 ± 0.09	3.97 ± 0.06	1.11 ± 0.09	2.12 x 10^{2}
	1.0	7.80 ± 0.08	4.09 ± 0.06	1.75 ± 0.16	2.08 x 10^{-2}
	2.0	7.93 ± 0.15	4.05 ± 0.09	1.62 ± 0.17	4.50 x 10^{-2}
1.0*M* H_2SO_4	5.0	8.12 ± 0.11	3.97 ± 0.07	1.39 ± 0.10	2.51 x 10^{-2}
	10.0	8.20 ± 0.10	3.95 ± 0.06	1.29 ± 0.09	2.00 x 10^{-2}
	20.0	8.34 ± 0.04	3.88 ± 0.03	1.16 ± 0.04	3.07 x 10^{-3}
	50.0	8.41 ± 0.07	3.88 ± 0.05	1.23 ± 0.08	1.23 x 10^{-2}

TABLE 3

PARAMETERS OBTAINED FROM THE DEOXYGENATED DATA BY EXPRESSION V AND THE LEAST SQUARES METHOD

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
(a)			
G^o	7.25 ± 0.04	7.51 ± 0.08	7.56 ± 0.09
G_x	0.39 ± 0.04	0.43 ± 0.04	0.42 ± 0.04
k_5/k_4	$(3.38 \pm 0.95) \times 10^{-4}$ (SVA)*		
variance	3.62×10^{-3}		
(b)			
G^o	7.25 ± 0.04	7.55 ± 0.04	7.59 ± 0.04
G_x	0.42 ± 0.02 (SVA)*		
k_5/k_4	$(3.86 \pm 0.69) \times 10^{-4}$		
variance	3.41×10^{-3}		

* SVA means single value assumed.

TABLE 4

PARAMETERS OBTAINED FROM ALL THE DATA BY EXPRESSION VI AND THE LEAST SQUARES METHOD

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
G^o	7.30 ± 0.06	7.62 ± 0.06	7.63 ± 0.06
G_R	3.35 ± 0.05	3.54 ± 0.04	3.59 ± 0.04
G_x	0.37 ± 0.02 (SVA)		
k_1/k_2	$(1.18 \pm 0.03) \times 10^{-3}$		
k_3/k_4	2.67 ± 0.9		
k_5/k_4	$(3.77 \pm 0.9 \times 10^{-4}$		
variance	2.30×10^{-2}		

TABLE 5

(a) PARAMETERS OBTAINED BY THE LEAST SQUARES METHOD ASSUMING EXPRESSION VI

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
G^o	7.22 ± 0.07	7.73 ± 0.05	7.78 ± 0.10
G_R	2.97 ± 0.09	3.65 ± 0.03	3.64 ± 0.05
G_x	0.50 ± 0.04	0.40 ± 0.03	0.30 ± 0.04
k_1/k_2	$(1.19 \pm 0.08) \times 10^{-3}$	$(1.20 \pm 0.05) \times 10^{-3}$	$(1.22 \pm 0.05) \times 10^{-3}$
k_3/k_4	$(2.9 \pm 1.6) \times 10^{1}$	1.5 ± 0.05	4.3 ± 3.0
k_5/k_4	$(5.3 \pm 2.1) \times 10^{-4}$	$(1.3 \pm 0.4) \times 10^{-3}$	$(5.6 \pm 3.0) \times 10^{-4}$
variance	1.34×10^{-2}	1.61×10^{-2}	1.57×10^{-2}

(b) PARAMETERS OBTAINED BY THE LEAST SQUARES METHOD ASSUMING EXPRESSION VIII

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
G^o	7.21 ± 0.08	7.80 ± 0.05	7.80 ± 0.11
G_R	3.34 ± 0.09	3.71 ± 0.03	3.67 ± 0.08
G_x	0.33 ± 0.05	0.38 ± 0.04	0.29 ± 0.06
k_1/k_2	$(1.08 \pm 0.04) \times 10^{-3}$	$(1.14 \pm 0.05) \times 10^{-3}$	$(1.22 \pm 0.05) \times 10^{-3}$
k_3/k_4	5.7 ± 4.3	1.55 ± 0.49	3.9 ± 2.9
k_5/k_4	$(1.77 \pm 1.0) \times 10^{-4}$	$(2.14 \pm 0.88) \times 10^{-3}$	$(5.98 \pm 3.4) \times 10^{-4}$
$k_6[H^+]/k_2$	$(0.87 \pm 0.25) \times 10^{-6}$	$(0.35 \pm 0.12 \times 10^{-6}$	$(0.07 \pm 0.18) \times 10^{-6}$
variance	1.01×10^{-2}	1.33×10^{-2}	1.60×10^{-2}

TABLE 6

PARAMETERS EVALUATED FROM THE COMBINED DATA USING EXPRESSION IX

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
G_R	3.31 ± 0.02	3.51 ± 0.02	3.56 ± 0.02
k_{11}/k_{12}	$(0.87 \pm 0.07) \times 10^{-3}$	$(0.94 \pm 0.06) \times 10^{-3}$	$(1.09 \pm 0.05) \times 10^{-3}$
G_X	0.31 ± 0.02	(SVA)*	
k_3/k_4	11.4 ± 3.0		
k_5/k_4	$(1.2 \pm 0.3) \times 10^{-3}$		
k_{-6}/k_{12}	$(4.6 \pm 3.5) \times 10^{-6}$		
k_6/k_1	$(1.8 \pm 1.3) \times 10^{-2}$		
k_2/k_1	$(2.6 \pm 1.6) \times 10^{2}$		
variance	1.96×10^{-2}		

* Single value assumed.

TABLE 7

PROPORTION OF EACH FERROUS SPECIES PRESENT IN THE DIFFERENT ACID SOLUTIONS

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
% $[Fe^{2+}]/\Sigma[Fe]$	60.9	66.9	65.8
% $[FeHSO_4^+]/\Sigma[Fe]$	2.0	9.8	14.0
% $[FeSO_4]/\Sigma[Fe]$	37.0	23.3	20.2
Mean charge	1.24	1.43	1.46

$\Sigma[Fe]$ = the total concentration of all forms of ferrous ion

TABLE 8

(a) PARAMETERS OBTAINED FROM DEOXYGENATED DATA WITH EXPRESSION XI

	$0.04M\ H_2SO_4$/ $0.10M\ Na_2SO_4$	$0.4M\ H_2SO_4$	$1.0M\ H_2SO_4$
G^o	7.08 ± 0.04	7.57 ± 0.04	7.69 ± 0.04
C	2.09 ± 0.13		
variance	6.57×10^{-3}		

(b) PARAMETERS OBTAINED FROM COMBINED DATA WITH EXPRESSION XII

G_R	3.25 ± 0.02	3.48 ± 0.02	3.53 ± 0.02
k_1/k_2	$(1.08 \pm 0.03) \times 10^{-3}$		
C	1.42 ± 0.13		
D	3.58 ± 0.20		
variance	3.23×10^{-2}		

TABLE 9

PARAMETERS OBTAINED FROM COMBINED DATA USING EXPRESSION XIII

	$0.04M\ H_2SO_4$/ $0.10M\ Na_2SO_4$	$0.4M\ H_2SO_4$	$1.0M\ H_2SO_4$
G_R	3.31 ± 0.02	3.52 ± 0.02	3.58 ± 0.02
k_{31}/k_{32}	$(0.87 \pm 0.07) \times 10^{-3}$	$(0.81 \pm 0.06) \times 10^{-3}$	$(0.94 \pm 0.05) \times 10^{-3}$
$C_{(Fe)}$	0.90 ± 0.13		
$D_{(O_2)}$	3.07 ± 0.18		
k_{-36}/k_{32}	$(5.3 \pm 2.7) \times 10^{-6}$		
k_{36}/k_1	$(6.5 \pm 3.3) \times 10^{-3}$		
k_2/k_1	$(2.4 \pm 1.0) \times 10^{2}$		
variance	2.19×10^{-2}		

TABLE 10

PARAMETERS OBTAINED FROM ALL THE DATA USING EXPRESSION XVI

	0.04*M* H_2SO_4/ 0.10*M* Na_2SO_4	0.4*M* H_2SO_4	1.0*M* H_2SO_4
G_R	3.07 ± 0.05	3.18 ± 0.05	3.18 ± 0.05
k_1/k_2	$(1.14 \pm 0.03) \times 10^{-3}$		
α	$(1.38 \pm 0.54) \times 10^{3}$		
β	$(2.63 \pm 0.90) \times 10^{5}$		
G_{cp}	0.69 ± 0.05		
variance	2.22×10^{-2}		

NOTES

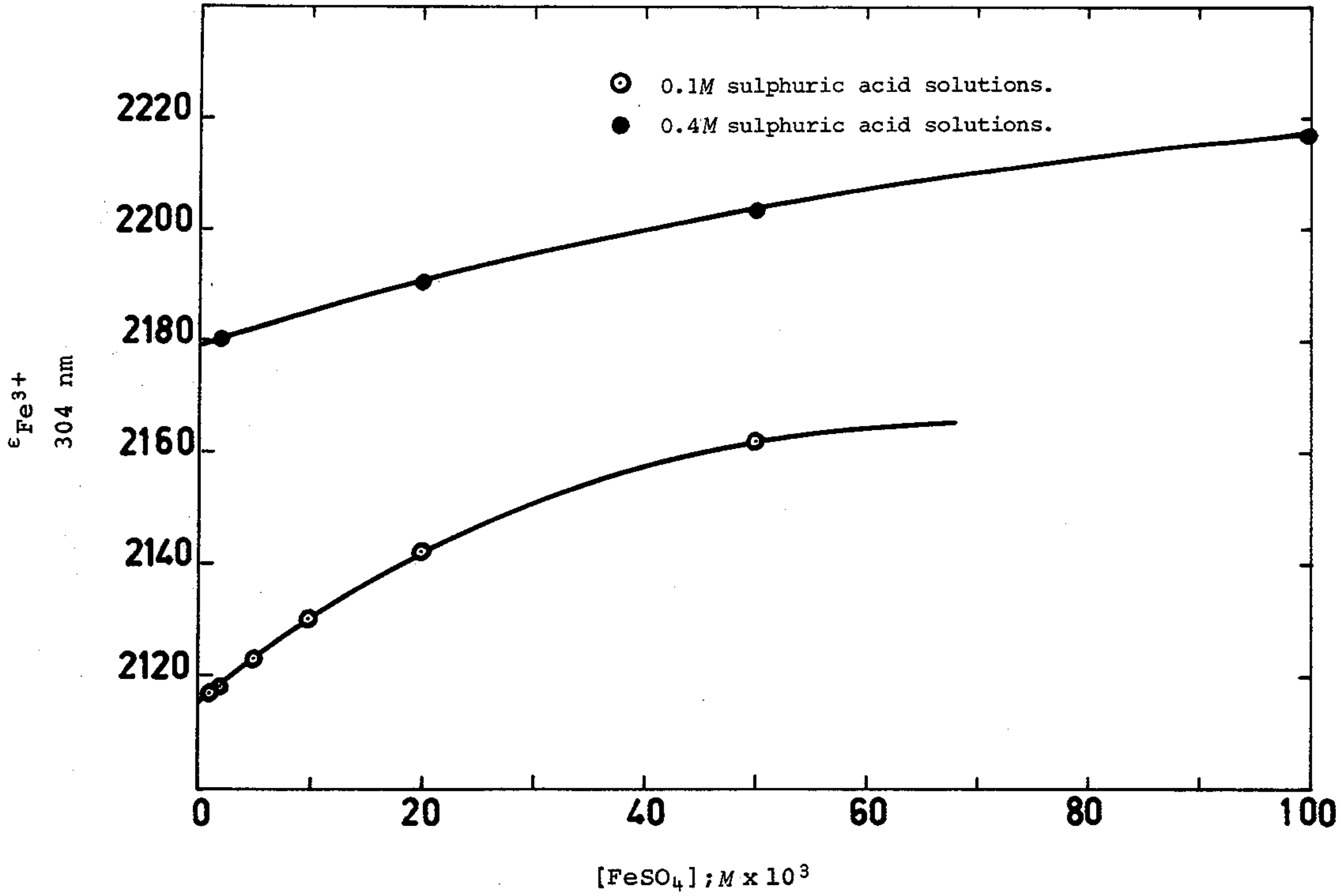

FIGURE 1. MOLAR EXTINCTION COEFFICIENT OF FERRIC ION AT 304 nm & 25°C VERSUS FERROUS SULPHATE CONCENTRATION

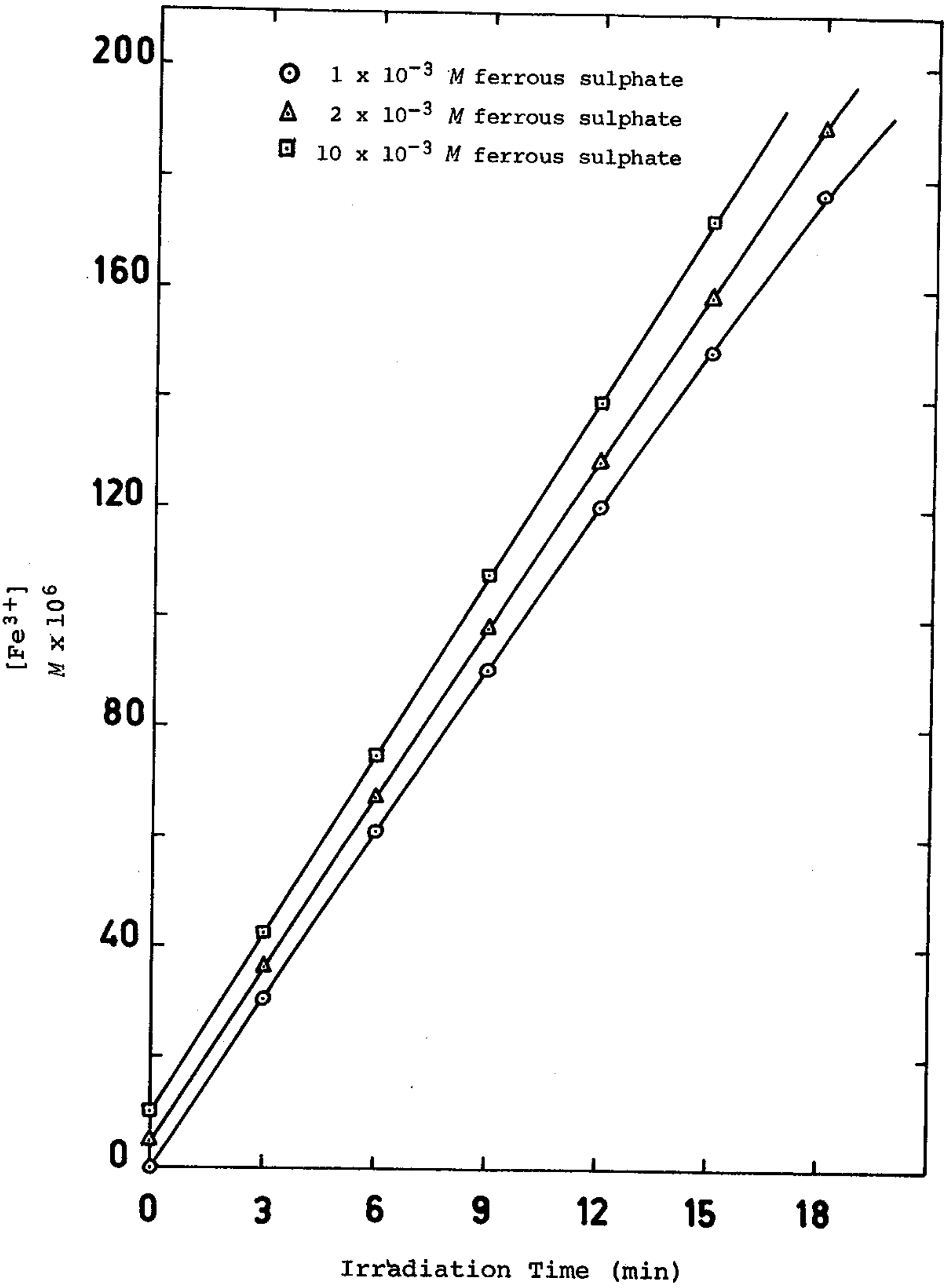

FIGURE 2. FERRIC ION CONCENTRATION VERSUS IRRADIATION TIME, DEOXYGENATED FERROUS SULPHATE SOLUTIONS IN 0.4$\underline{M}$ H_2SO_4/0.1$\underline{M}$ Na_2SO_4 SOLUTION, DOSE RATE ~1 krad min^{-1}

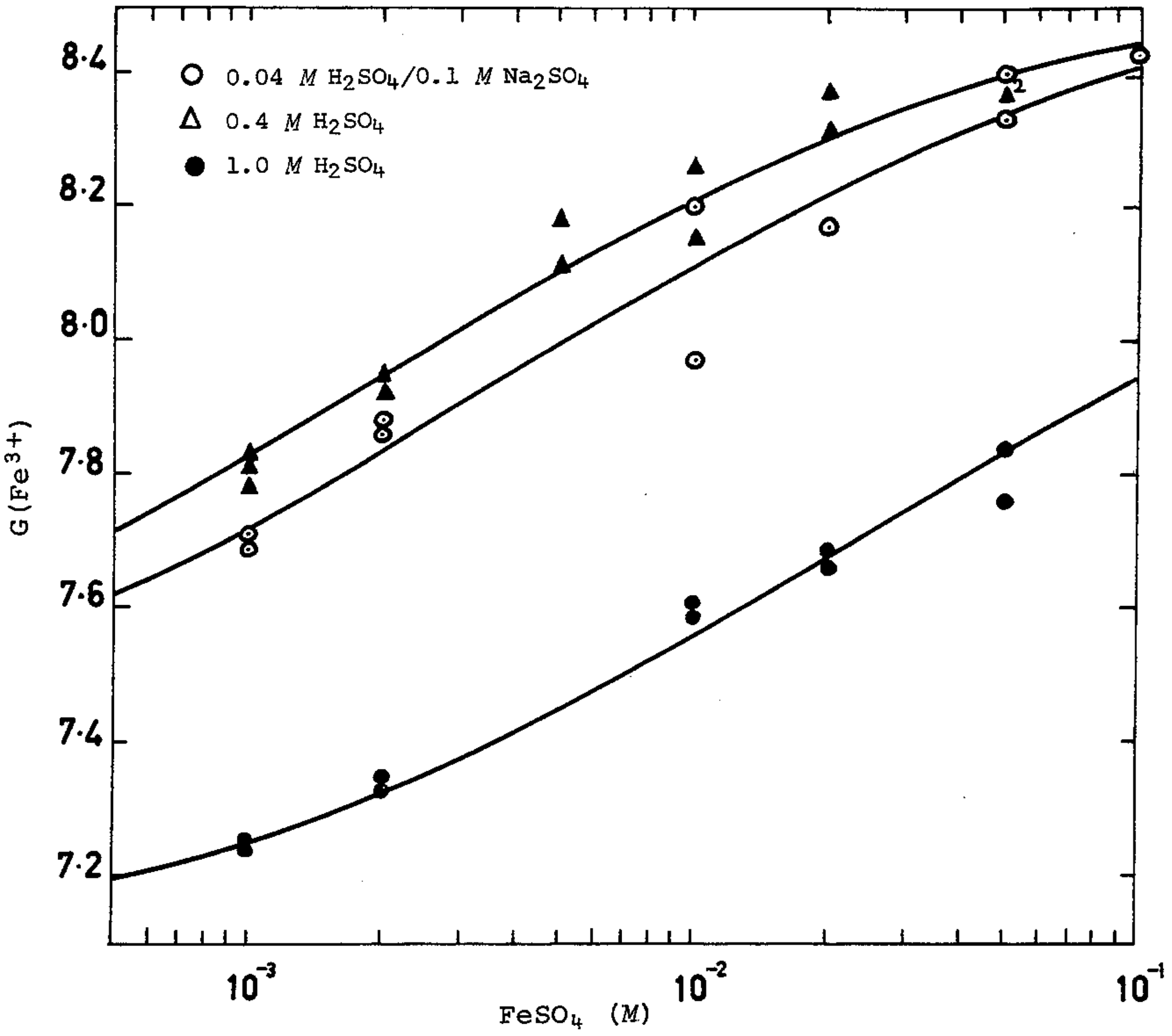

FIGURE 3. G(Fe^{3+}) FOR DEOXYGENATED SOLUTIONS VERSUS FERROUS SULPHATE CONCENTRATION

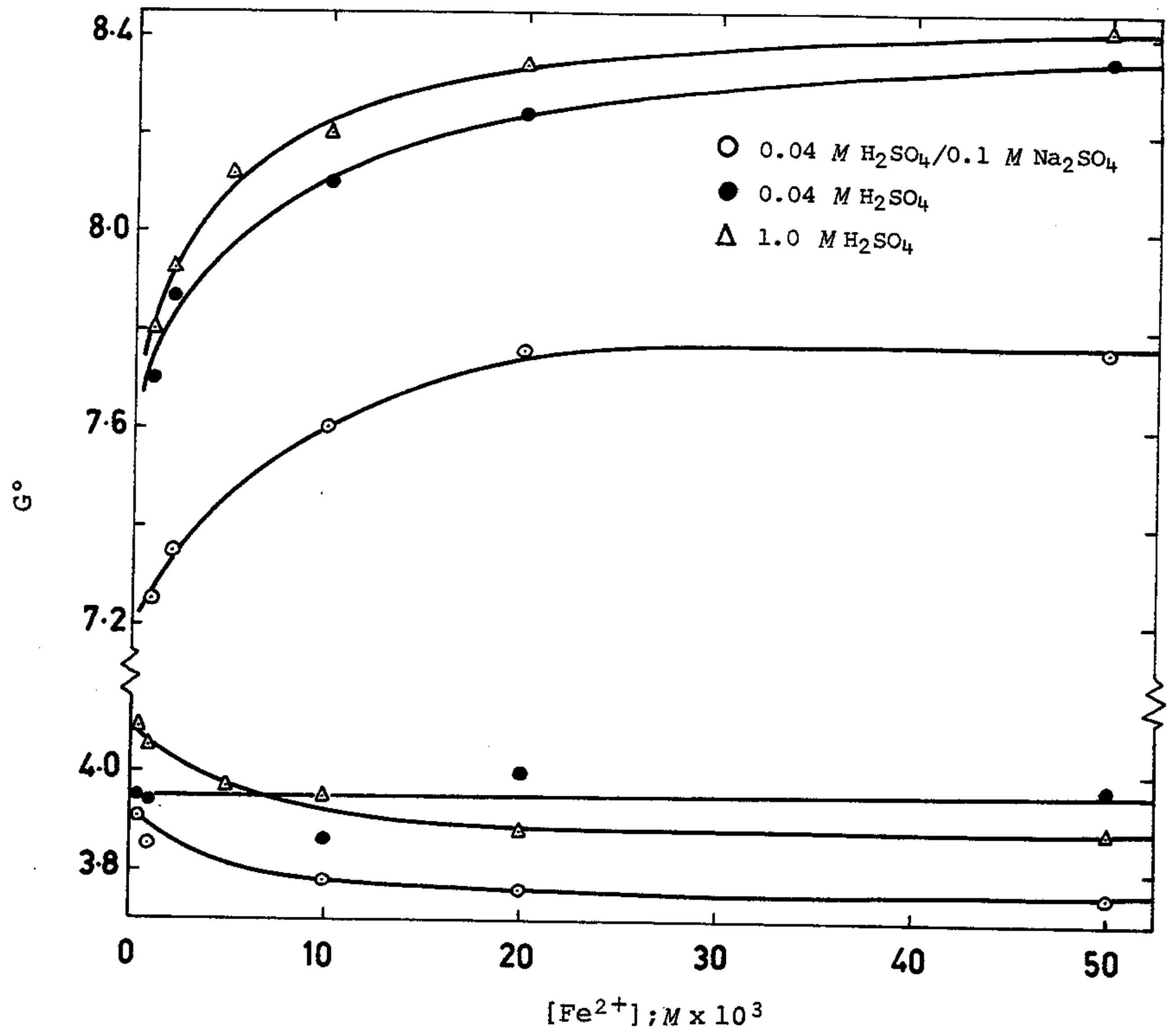

FIGURE 4. G° AND G_R VERSUS FERROUS SULPHATE CONCENTRATION, ALL SOLUTIONS

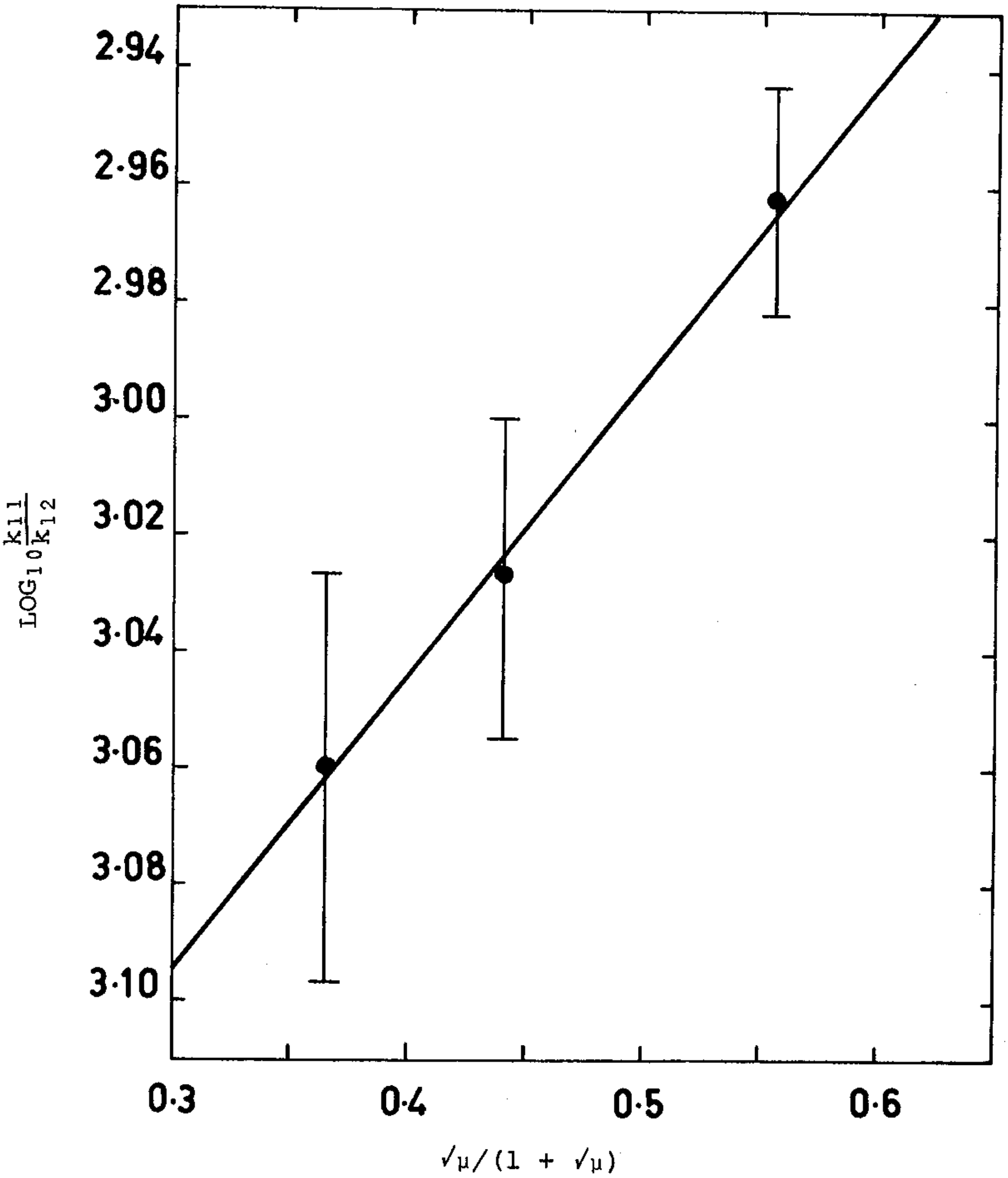

FIGURE 5. $\log_{10} k_{11}/k_{12}$ VERSUS $\sqrt{\mu}/(1 + \sqrt{\mu})$