An investigation into the kinetics and mechanism of the oxidation of iron (II) by oxygen in aqueous chloride solutions

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SYNOPSIS

A reaction mechanism for the oxidation of ferrous chloride by molecular oxygen is developed, and the appropriate constants are evaluated. The effect of a number of cations and anions on the rate of oxidation has been tested.

SAMEVATTING

Die reaksiemeganisme vir die oksidasie van ferrochloried by molekulêre suurstof is ontwikkel en die afsonderlike konstantes bereken. Die invloed van 'n aantal katione en anione op die tempo van oksidasie is getoets.

INTRODUCTION

The hydrometallurgical treatment of base metals by ferric chloride requires the oxidation of ferrous chloride as one of its unit operations. In order that an accurate design procedure for this operation may be developed, a knowledge of the oxidation kinetics is necessary. Hydrometallurgical liquors contain various anions and cations that may affect the oxidation process, and a knowledge of these effects is essential.

A search through the literature reveals that there is uncertainty about the reaction mechanism for iron (II) oxidation, and the order of the reaction itself has still not been conclusively established. At best, empirical relations are used to describe the kinetics under given conditions, and these relations can be applied only to similar conditions. The work reported covers a fairly wide range of conditions, but no set is applicable to those envisaged for the hydrometallurgical process. Variables such as hydrogen-ion concentration and chloride-ion concentration have not been studied in a manner that permits their separate effects to be evaluated accurately.

A reaction scheme has therefore been developed that incorporates the effects of the main reactants, namely, the ferrous and chloride ions, their complexes, and oxygen. The kinetics of this reaction scheme and the appropriate constants have been evaluated for the working conditions encountered in hydrometallurgy. The effects due to a number of cations and anions likely to be present in practice were investigated, although the mechanisms by which catalysis occurred were not determined.

LITERATURE SURVEY

Lamb and Elder[1] investigated the oxidation of ferrous sulphate at various acid concentrations in the range 0 to 5M H_2SO_4 and concluded that the reaction was extremely slow. Posner[2] confirmed their results and also investigated the reaction for acid concentrations in the range 4N to 8N HCl. He concluded that the reaction rate was first order with respect to iron (II) concentration and oxygen concentration, and had a functional dependency on the hydrochloric acid concentration. He developed a reaction mechanism based on the Haber-Weiss mechanism[3] and used this to explain his results.

George[4] investigated the oxidation of iron (II) in perchloric acid and found the reaction to be second order with respect to the iron (II) concentration, and first order with respect to the oxygen concentration. He also found that the third-order rate constant increased slightly with increasing hydrogen-ion concentration and incorporated this effect in his reaction scheme.

Sobkowski[5] investigated the oxidation of ferrous ions in perchloric acid by hydrogen peroxide. Basing his work on a modified Haber-Weiss scheme, he showed that the reaction was first order with respect to the iron (II) concentration.

Lepin and Matseevskii[6] showed that the oxidation of iron (II) in chloride media was second order with respect to the iron (II) concentration and that the rate increased with increasing chloride-ion concentration. They concluded that this increase was due to the formation of more-reactive complexes.

Sysoeva et al.[7] investigated the oxidation of iron (II) at pH values greater than 3,0. They found that the reaction was first order with respect to the iron (II) concentration and was catalysed by the addition of cupric ions. In the pH range they investigated, they showed that the hydroxyl-ion concentration affected the reaction rate, and they proposed an empirical relation for the dependence of the rate constant on the hydroxyl-ion concentration. In their introduction they commented on the order of the reaction with respect to the iron (II) concentration and concluded that variations in experimental conditions had been responsible for the finding of both first-order and second-order dependence.

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Ermilov et al.[8] showed that the oxidation of ferrous chloride was first order with respect to the iron (II) concentration. However, the rate constant was a function of the ratio of the iron (II) concentration to the iron (III) ion concentration, and they ascribed this dependence to the formation of complex ions at given ratios. They showed that the reaction rate increased substantially with both temperature and acid concentration, and they developed empirical relations to describe this dependence. They attempted to develop a reaction scheme to describe the process but did not use the scheme in a final analysis of the system.

Sysoeva and Rotinyan[9] proposed reaction schemes for the oxidation of iron (II) in the presence of sulphate ions at various pH values, and concluded that the reaction rate was generally first order with respect to the iron (II) concentration and the oxygen concentration.

KINETIC MODEL

The oxidation of iron (II) to iron (III) in chloride media is considered to occur according to the following mechanism.

$$Fe^{2+} + O_2 \overset{\mathrm{Ke}}{\rightleftharpoons} Fe^{2+}.O_2 \quad \ldots\ldots\ldots\ldots \quad \mathrm{I}$$

$$Fe^{2+}.O_2 + Fe^{2+} \xrightarrow{k_{\mathrm{II}}} 2Fe^{3+} + O_2^{2-} \quad \ldots\ldots\ldots \quad \mathrm{II}$$

$$H^+ + O_2^{2-} \rightleftharpoons HO_2^- \quad \ldots\ldots\ldots\ldots \quad \mathrm{III}$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad \ldots\ldots\ldots\ldots \quad \mathrm{IV}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+} \quad \ldots\ldots \quad \mathrm{V}$$

$$Fe^{2+} + OH \rightarrow OH^- + Fe^{3+} \quad \ldots\ldots\ldots \quad \mathrm{VI}$$

Reaction I, a fast equilibrium reaction, was proposed by George[4] for the oxidation of iron (II) in perchloric acid. Reactions IV to VI are a modification of the Haber-Weiss mechanism[3], proposed by Posner[2], and reactions II and III are now proposed as possible steps necessary to produce the scheme I to VI.

Reaction II is the rate-controlling step, and thus

$$\frac{-d(Fe^{2+})}{dt} = 2k_{\mathrm{II}}\,(Fe^{2+}.O_2)\,(Fe^{2+}).$$

Reaction I represents a rapid equilibrium such that

$$Ke = \frac{(Fe^{2+}\cdot O_2)}{(Fe^{2+})(O_2)}$$

Therefore,

$$\frac{-d(Fe^{2+})}{dt} = 2k_{\mathrm{II}}\,Ke\,(Fe^{2+})^2(O_2)\cdot \quad \ldots\ldots\ldots \quad (1)$$

In chloride media, however, the ferrous chloride complexes exist, the concentrations being determined in accordance with the stability constants K_1 and K_2, as follows:

$$K_1 = \frac{(FeCl^+)}{(Fe^{2+})\,(Cl^-)}$$

and

$$K_2 = \frac{(FeCl_2)}{(FeCl^+)\,(Cl^-)}\,.$$

These resolve to give the following relation:

$$(Fe^{2+}) = \frac{(Fe^{2+})_T}{\{1+K_1\,(Cl^-)+K_1K_2(Cl^-)^2\}} \quad \ldots\ldots \quad (2)$$

$$(FeCl^+) = \frac{(Fe^{2+})_T\,K_1(Cl^-)}{\{1+K_1\,(Cl^-)+K_1K_2\,(Cl^-)^2\}} \quad \ldots\ldots \quad (3)$$

$$(FeCl_2) = \frac{(Fe^{2+})_T\,K_1K_2\,(Cl^-)^2}{\{1+K_1\,(Cl^-)+K_1K_2\,(Cl^-)^2\}}\,, \quad \ldots\ldots \quad (4)$$

where $(Fe^{2+})_T$ is the concentration of iron (II) present both free and complexed.

Thus, equations I and II of the proposed reaction scheme can be expressed in general terms as follows:

$$Fe\,(II)_i + O_2 \overset{Ke_i}{\rightleftharpoons} Fe\,(II)_i.O_2$$

$$Fe\,(II)_i.O_2 + Fe\,(II)_j \xrightarrow{k_{i_j}} Fe\,(III)_i + Fe\,(III)_j + O_2^{2-},$$

where $i = 1, 2, 3$,

$j = 1, 2, 3$, and

$Fe\,(II)_1 = Fe^{2+}$, $Fe\,(II)_2 = FeCl^+$, $Fe\,(II)_3 = FeCl_2$.

Thus,

$$-\left(\frac{1}{O_2}\right)\cdot\frac{d(Fe^{2+})_T}{dt}$$

$$= 2 \sum_{i=1}^{3} \sum_{j=1}^{3} Ke_i\,k_{ij}\,(Fe\,(II)\cdot(Fe\,(II)_j).$$

When equations 2,3, and 4 are used, this expression reduces to the form

$$-\left(\frac{1}{O_2}\right)\frac{d(Fe^{2+})_T}{dt}$$

$$= \frac{\left\{k_o + \sum_{i=1}^{4} ki(Cl^-)^i\right\}(Fe^{2+})^2{}_T}{\{1+K_1(Cl^-)+K_1K_2(Cl^-)^2\}^2}\,, \quad \ldots\ldots\ldots\ldots \quad (5)$$

where $k_o = k_o(T)$,

$k_i = k_i(T)$ and is a general constant incorporating equilibrium constants, stability constants, and reaction rate constants,

$K_1 = K_1(T)$,

$K_2 = K_2(T)$.

Also

$$(Cl^-)_T = (Cl^-) + (Fe^{2+})_T \times$$

$$\left\{\frac{K_1(Cl^-)+2\,K_1K_2\,(Cl^-)^2}{1+K_1(Cl^-)+K_1K_2\,(Cl^-)^2}\right\} \quad \ldots\ldots \quad (6)$$

EXPERIMENTAL PROCEDURE

The essential feature of the experimental procedure adopted was that the concentrations of the ferrous and chloride species remained constant throughout. This was achieved by saturating the solution with oxygen and monitoring the oxygen concentration in solution with an oxygen sensor. As the initial oxygen concentration was of the order to 12 to 15 p.p.m., the change in reactant concentrations was negligible. This permitted the determination of the dependence of the iron (II) oxidation reaction on oxygen, iron (II), and chloride-ion concentrations and on temperature.

The experimental apparatus consisted of a glass reaction vessel of 15 ml capacity suspended in a constant-temperature bath. The design of bath and reactor was such that constant stirring could be achieved in the reactor by means of a magnetic follower. A YSI model 5331 Oxygen Sensor was used; this fitted neatly into the reactor and effectively sealed the reacting liquid from the atmosphere. The output from the sensor was recorded directly onto a graph plotter via a current-voltage converter.

Solutions were made up from analytical grades of ferrous chloride, sodium chloride, hydrochloric acid, iron wire, and perchloric acid. This procedure permitted the independent variation of the concentrations of ferrous ion, chloride ion, or hydrogen ion, although no samples containing both chloride and perchloric ions were prepared. The iron (II) concentration was determined by titrating with dichromate, and the chloride concentration by means of an automatic titrimeter using silver nitrate. When catalysed runs were investigated, the cations were added as A.R.-grade chlorides, and the anions as A.R.-grade sodium salts.

The required temperature was selected, and approximately 8 ml of solution was introduced into the reactor. The oxygen sensor was inserted, the stirrer was set in motion, and the apparatus was allowed to reach a constant temperature.

The solution was then saturated with oxygen, and the oxygen probe inserted into the solution, preventing further exposure of the solution to gaseous oxygen. The output from the sensor was recorded continuously, until the oxygen concentration had reached a negligible value. As the output of the sensor was directly proportional to the oxygen concentration in solution, the trace obtained was essentially a plot of oxygen concentration against time. For all experiments, a plot of log $(V(t)/V\infty(t))$ against t was constructed, where $V\infty(t)$ was the final sensor output and $V(t)$ the value at any time t. The advantage of this plot was that no calibration of the oxygen sensor was necessary. In all cases, a linear dependence existed, indicating that the reaction mechanism was first order with respect to the oxygen concentration. The slope of the plot uniquely established the rate dependence due to the iron (II) ion and chloride-ion concentrations and any catalysts present.

RESULTS

The experimental results pertaining to the uncatalysed oxidation of iron (II) at a hydrogen-ion concentration of 0,1 moles per litre are tabulated in Tables I to IV.

In the experimental work, the oxygen sensor effectively measured the change of oxygen concentration with respect to time. In all cases, the mechanism is first order with respect to oxygen, and hence the following relation holds:

$$-\frac{d(O_2)}{dt}=k_{ex}\,(O_2).$$

The stoichiometry of the oxidation reaction gives

$4\ FeCl_2+4\ HCl+O_2 \rightarrow 4\ FeCl_3+2H_2O.$

Therefore, provided that all the oxygen reacts to form water,

$$-\frac{d(Fe^{2+})}{dt}=4.k_{ex}\,(O_2).$$

TABLE I

OXIDATION RATE OF IRON (II) IN PERCHLORIC ACID AT CONSTANT IRON (II) CONCENTRATION AND DIFFERENT TEMPERATURES

Total iron (II) concentration (mol/l)	$k_{app}\times 10^3$ measured rate constant s^{-1}	$k^1{}_{app}\times 10^3$ corrected rate constant $l^2/(mol^2s)$	Temp. °C
1,136	3,836	2,973	36,2
1,144	3,900	2,980	36,2
0,494	1,816	7,442	51,0
0,729	4,020	7,564	51,0
0,976	7,152	7,508	51,0
1,024	7,912	7,545	51,0
1,223	11,120	7,434	51,0
1,464	15,924	7,430	51,0
0,685	8,576	18,276	66,2
0,783	10,816	17,642	66,2
0,847	12,728	17,742	66,2
0,914	14,640	17,524	66,2

TABLE II

OXIDATION RATE OF IRON (II) IN CHLORIDE MEDIUM, MEASURED AT CONSTANT IRON (II) AND CHLORIDE-ION CONCENTRATIONS AND AT 36,2 °C

Total iron (II) concentration mol/l	Total chloride-ion concentration mol/l	$k_{app}\times 10^2$ measured rate constant s^{-1}	$k^1{}_{app}\times 10^2$ corrected rate constant $l^2/(mol^2s)$
0,484	1,970	0,179	0,765
0,484	2,992	0,303	1,293
0,484	3,940	0,452	1,930
0,484	4,920	0,907	3,445
0,726	2,510	0,435	0,825
0,726	2,950	0,564	1,070
0,726	4,920	1,762	3,361
0,968	1,970	0,558	0,596
0,968	2,992	0,979	1,045
0,968	3,940	1,862	1,987
0,968	4,920	3,158	2,970
1,210	2,950	1,296	0,885
1,210	3,940	2,593	1,651
1,210	4,920	4,821	2,893

TABLE III

OXIDATION RATE OF IRON (II) IN CHLORIDE MEDIUM, MEASURED AT CONSTANT IRON (II) AND CHLORIDE-ION CONCENTRATIONS AND AT 51,0 °C

Total iron (II) concentration mol/l	Total chloride-ion concentration mol/l	$k_{app}\times 10^2$ measured rate constant s^{-1}	$k^1{}_{app}\times 10^2$ corrected rate constant $l^2/(mol^2s)$
0,488	1,070	0,269	1,131
0,488	2,044	0,505	2,122
0,488	3,016	1,039	4,364
0,488	3,988	1,793	7,528
0,488	4,960	3,332	13,992
0,732	1,558	0,713	1,330
0,732	2,044	0,983	1,835
0,732	3,016	1,872	3,493
0,732	3,988	3,509	6,548
0,732	4,960	6,533	12,192
0,976	2,048	1,659	1,742
0,976	2,980	3,160	3,317
0,976	3,980	5,487	5,760
0,976	4,470	7,689	8,072
0,976	4,960	9,697	10,180
1,464	3,118	6,794	3,170
1,464	3,602	8,916	4,160
1,464	4,088	11,261	5,256
1,464	4,960	16,812	7,844

TABLE IV

OXIDATION RATE OF IRON (II) IN CHLORIDE MEDIUM, MEASURED AT CONSTANT IRON (II) AND CHLORIDE-ION CONCENTRATIONS AND AT 66,2 °C

Total iron (II) concentration mol/l	Total chloride-ion concentration mol/l	$k_{app}\times 10^2$ measured rate constant s^{-1}	$k^1{}_{app}\times 10^2$ corrected rate constant $l^2/(mol^2 s)$
0,484	1,064	0,665	2,841
0,484	1,970	1,339	5,716
0,484	2,992	2,582	11,020
0,484	3,378	3,588	15,316
0,484	3,667	4,062	17,340
0,484	3,940	5,115	21,836
0,726	1,546	2,011	3,816
0,726	2,510	3,894	7,388
0,726	2,950	5,547	10,524
0,968	1,970	4,483	4,784
0,968	2,510	6,422	6,606
0,968	2,992	8,302	8,860
0,968	3,667	12,935	13,804

Thus $\frac{1}{(O_2)}\cdot\frac{d(Fe^{2+})}{dt}=k_{app}=4\ k_{ex}$,

where k_{app} is the so-called "measured rate constant" tabulated in Tables I to IV.

George[4] showed that, in perchloric acid, the rate of oxidation was second order with respect to the iron (II) concentration. Thus,

$$k^1_{app}=\frac{k_{app}}{(Fe^{2+})_T{}^2},$$

where $k^1{}_{app}$ is the so-called "corrected rate constant" tabulated in Tables I to IV. As can be seen from Table V, second-order kinetics apply.

From the kinetic model derived earlier,

$$k^1_{app}=\frac{k_{app}}{(Fe^2{}_+)_T{}^2},\quad =\frac{k_o+\sum_{i=1}^{4}k_i\,(Cl^-)^i}{\{1+K_1(Cl^-)+K_1K_2(Cl^-)^2\}^2}\quad . \quad (7)$$

For the runs performed in the absence of chloride, the above equation reduces to

$$k^1_{app}=k_o$$
$$=k_{oo}T\exp\left(-\Delta E_o/RT\right),$$

where ΔE_o is the activation energy for the chloride-independent step.

This expression was solved using the mean values of $k^1{}_{app}$ tabulated in Table I, and the resulting values of k_{oo} and ΔE_o are shown in Table V (a).

TABLE V (a)

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE OXIDATION RATE CONSTANTS OF FERROUS AND FERROUS CHLORIDE COMPLEXES

	k_{io}	ΔE cal/mol
k_o	$2,026\times 10^3$	$1,1779\times 10^4$
k_1	$3,631\times 10^9$	$2,0626\times 10^4$
k_2	$3,389\times 10^8$	$1,9911\times 10^4$

TABLE V(b)

STABILITY CONSTANTS FOR THE FIRST AND SECOND FERROUS CHLORIDE COMPLEXES

	K_o	ΔH cal/mol
K_1	$2,5170\times 10^2$	$4,087\times 10^3$
K_2	$1,4144\times 10^{-1}$	$2,712\times 10^2$

To test the validity of the model in the presence of chloride ions, and to evaluate the corresponding parameters, two distinct operations are necessary.

From equation (7), it follows that a plot of $k^1{}_{app}$ against (Cl^-), which is the concentration of free chloride ion, should be a function of temperature only. Therefore, equation (7) can be written as

$$k^1{}_{app}=f\,(Cl^-)\quad .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ . \quad (8)$$

Also, the concentration of free chloride ion is related to the concentrations of total chloride ion and total iron (II) by the expression

$$(Cl^-)_T=(Cl^-)+(Fe^{2+})_T\ \frac{K_1(Cl^-)+2\ K_1K_2(Cl^-)^2}{1+K_1(Cl^-)+K_1K_2(Cl^-)^2}\quad .\ .\ .\ .\ .\ .\ .\ .\ . \quad (9)$$

The first operation involved the solution of equations (8) and (9) to determine the values of the stability constants K_1 and K_2. The technique adopted is as follows.

Powell's[10] search technique was used to search for the best values of K_1 and K_2. At each iteration, the values of K_1 and K_2 currently selected were used with each set of $(Cl^-)_T$ and $(Fe^{2+})_T$ to solve equation (9) for (Cl^-). This value of (Cl^-) corresponded to an experimentally determined value of $k^1{}_{app}$. A polynomial of three terms in free chloride ion (equation (8)) was then fitted to the generated data set $k^1{}_{app}$, (Cl^-), using the technique of Law and Bailey[11]. The sum-of-squares error between the observed rate constants $k^1{}_{app}$ and the computed values was then used by the Powell search routine to determine better values of the stability constants K_1 and K_2. This iterative procedure was continued until the minimum sum of squares had been obtained.

The procedure was carried out on the results obtained at 51 °C and 66,2 °C, using a chloride concentration range of 1,070M to 4,960M and an iron (II) concentration range of 0,484M to 0,976M. The values of the stability constants obtained were used to solve the expression

$$K=K_o\exp\left(-\Delta H/RT\right),$$

and the results are tabulated in Table V (b).

The second operation involved the determination of the overall-reaction rate constants. When the stability constants K_1 and K_2 and the overall-reaction rate constant k_o had been evaluated, equation (7) was then solved for the constants k_i, again using the technique of Law and Bailey. However, equation (7) had to be simplified, so that the number of parameters involved would be compatible with the number of experimental observations. It was assumed that the terms with $i=1$ and $i=2$ could be approximated by a term with $i=1$, and the terms with $i=3$ and $i=4$ could be approximated by an $i=4$ term. This procedure was also carried out on the results obtained at 51,0 and 66,2 °C, and the quality of the fits obtained is shown graphically in Figs. 1 and 2.

Thus, the model fitted to the data has the form

$$-\frac{1}{(O_2)}\cdot\frac{d(Fe^{2+})_T}{dt}=\frac{\{k_o+k_1(Cl^-)+k_2(Cl^-)^4\}(Fe^{2+})^2{}_T}{\{(1+K_1(Cl^-)+K_1K_2(Cl^-)^2\}^2},$$

where $k_i=k_{io}\,T\exp(-\Delta Ei/RT)$ $i=0,1,2$
and $K_j=K_{oj}\exp(-\Delta H_j/RT)$ $j=1,2$.

The corresponding values of the parameters are listed in Tables V (a) and V (b).

The data obtained at 51,0°C and 66,2°C were used to determine the activation energies and pre-exponential terms. These values were then used to predict the oxidation rates at 36,2 °C.

Figs. 3, 4, and 5 compare the regressed (dotted lines) and predicted (solid lines) first-order reaction rate constants with the experimentally determined first-order rate constant, k_{app}.

EFFECTS OF VARIOUS ANIONS AND CATIONS

In hydrometallurgical liquors, a number of cations and anions that may catalyse the oxidation process are present. The effect of these ions may, however, be other than kinetic because they may affect oxygen solubility, liquid surface tension, and other physical factors.

These experiments were undertaken to ascertain the kinetic effects only, and an analysis of the results was limited to expected trends.

TABLE VI

OXIDATION RATE OF FERROUS CHLORIDE CATALYSED BY CUPRIC CHLORIDE AT 51,0 °C

Total iron (II) concentration mol/l	Total chloride-ion concentration mol/l	Cu^{2+} concentration mol/l	$k_{app}\times10^2$ measured rate constant s^{-1}
0,726	1,596	0,0000	0,750*
		0,0035	2,156
		0,0091	3,760
		0,0105	4,876
		0,0140	5,400
		0,0210	6,480
0,726	2,078	0,0000	1,002*
		0,0035	3,768
		0,0091	6,396
		0,0105	8,944
		0,0140	11,516
		0,0210	13,352

*Predicted values

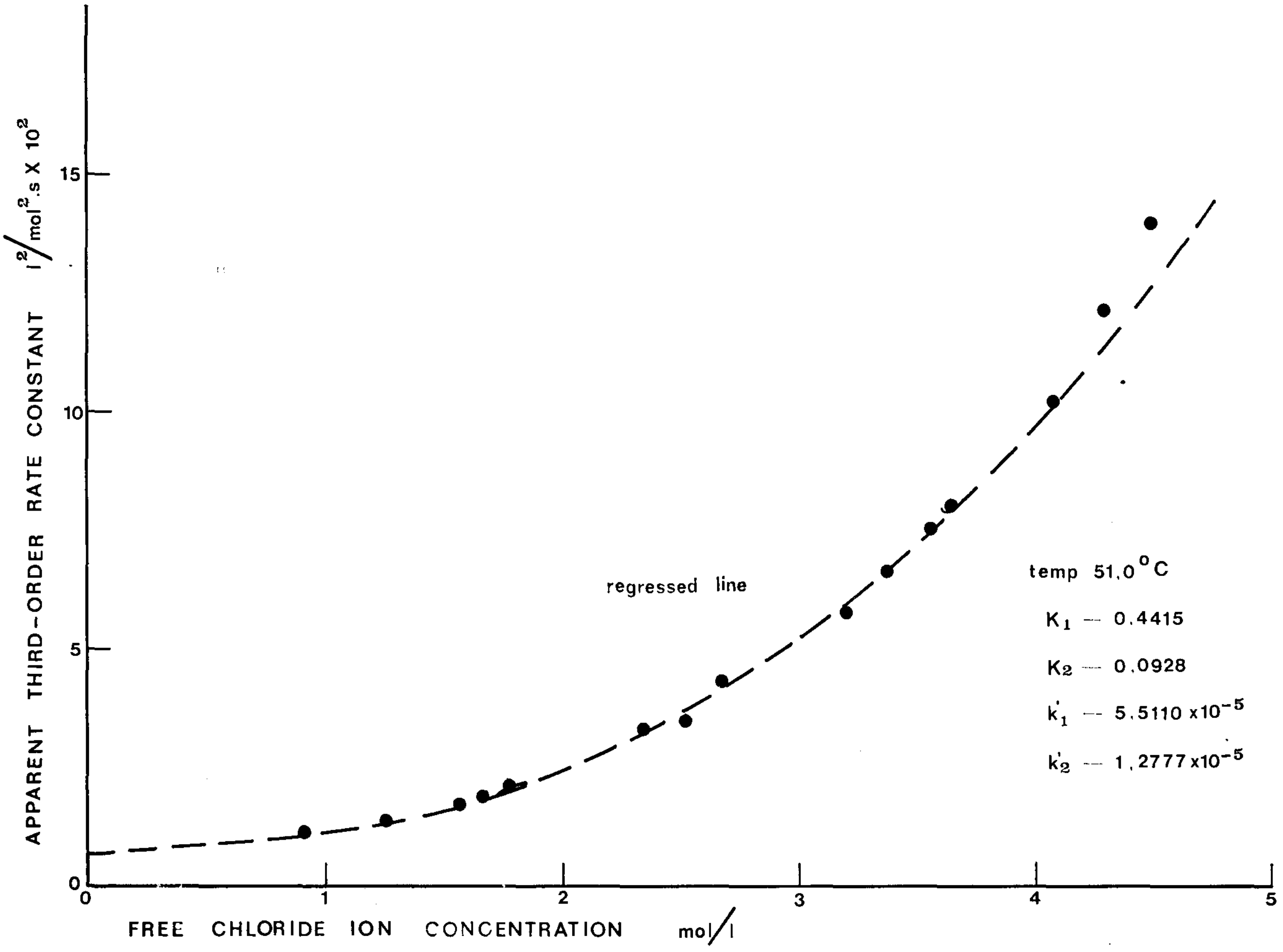

Fig. 1—The observed and predicted variation of the apparent third-order rate constant as a function of the free chloride ion concentration at 51,0 °C

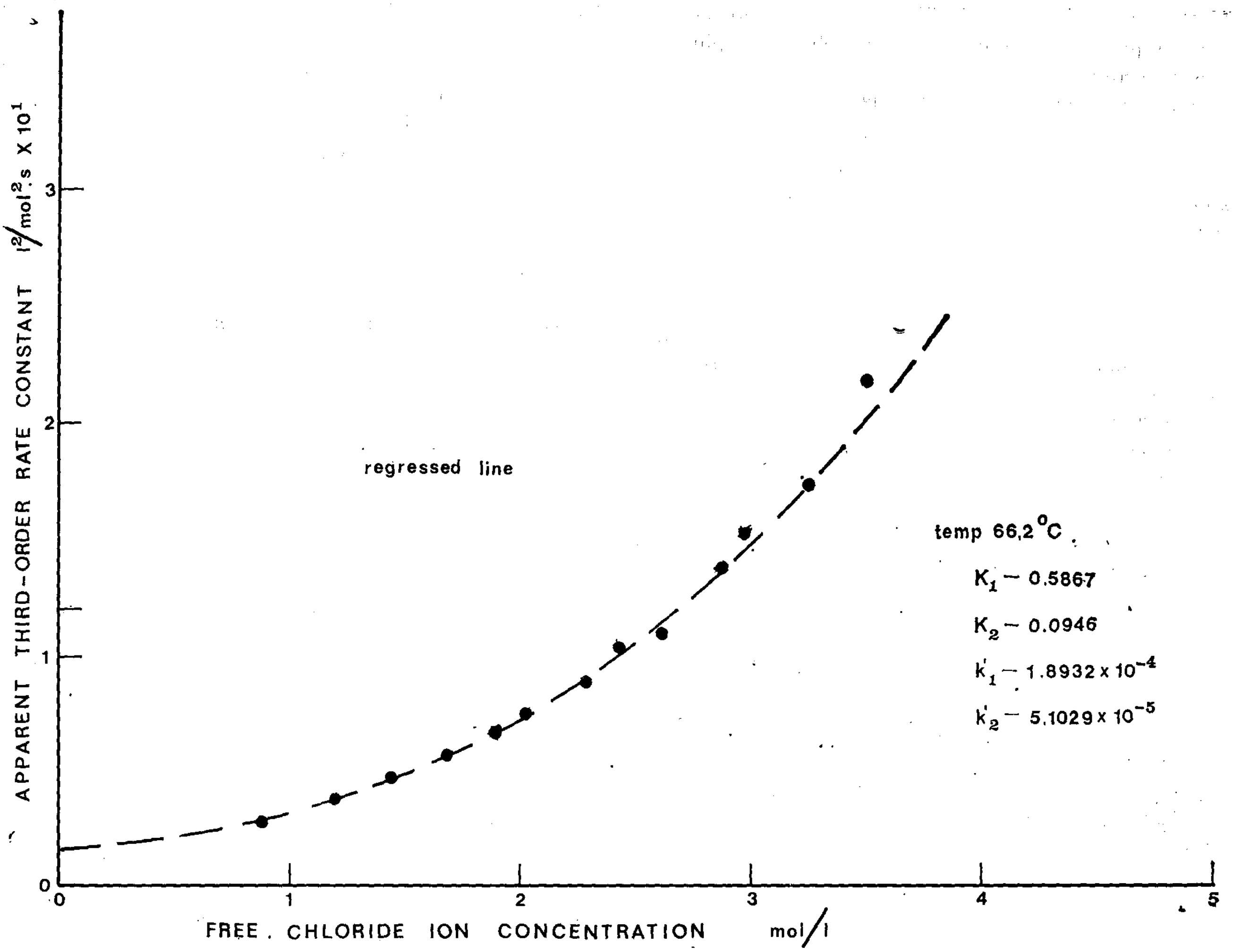

Fig. 2—The observed and predicted variation of the apparent third-order rate constant as a function of the free chloride ion concentration at 66,2°C

TABLE VII

OXIDATION RATE OF FERROUS CHLORIDE CATALYSED BY VARIOUS ANIONS AND CATIONS AT 51,0°C

Total iron (II) concentration mol/l	Total chloride-ion concentration mol/l	Catalyst	Catalyst concentration mol/l	$k_{app} \times 10^2$ measured rate constant s^{-1}
0,683	2,919	H^+	0,10	1,549
			0,39	1,400
			0,78	1,431
			1,17	1,515
			1,56	1,457
0,726	2,992	SO_4^{2-}	0,00	1,950
			0,10	1,865
			0,20	1,808
			0,50	1,765
0,726	2,992	NH_4^+	0,492	1,728
			0,984	1,525
			1,476	1,400
0,726	2,078	Zn^{2+}	0,0000	1,002
			0,0071	1,032
			0,0142	0,985
			0,0214	0,985
0,726	2,078	Ni^{2+}	0,0072	1,014
			0,0143	1,060
			0,0215	1,060

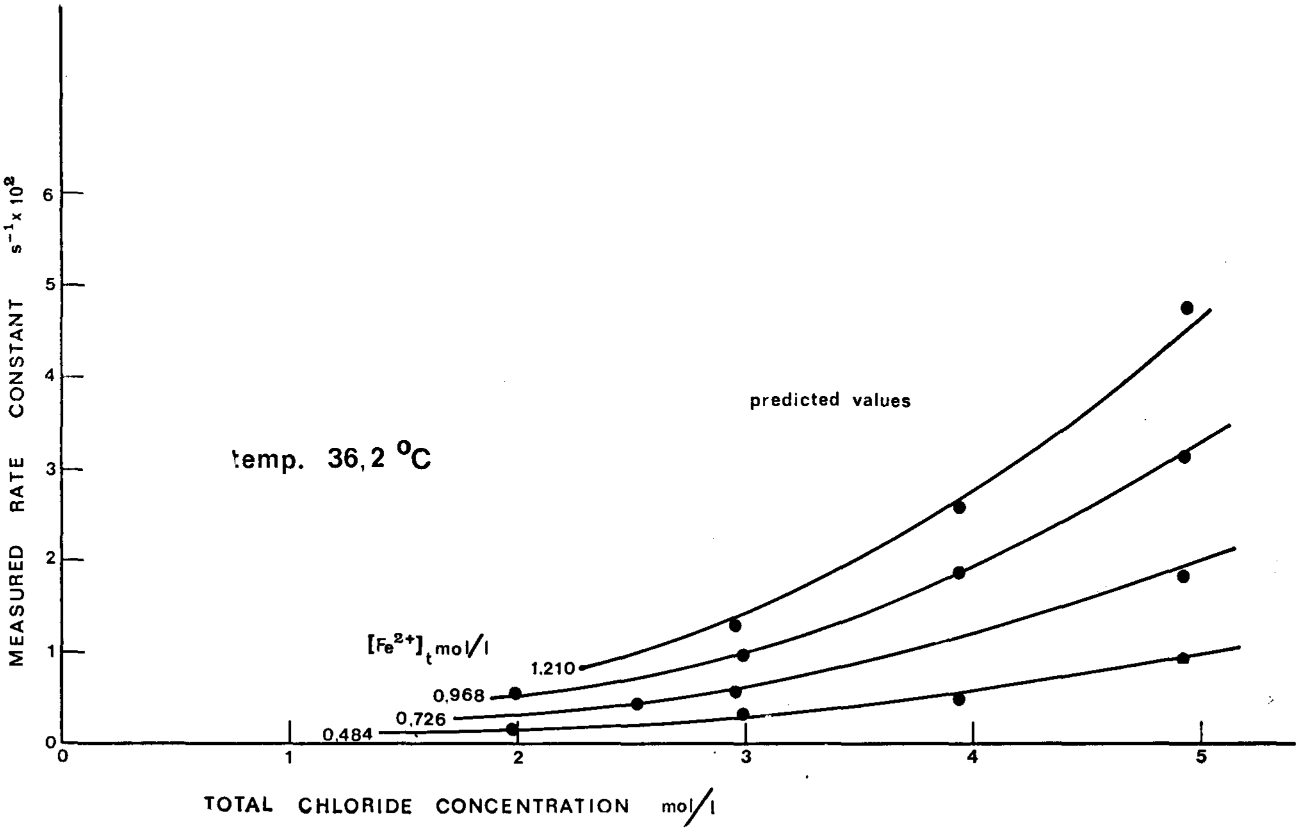

Fig. 3—Predicted rate constants at 36,2°C as a function of total chloride concentration and ferrous concentration

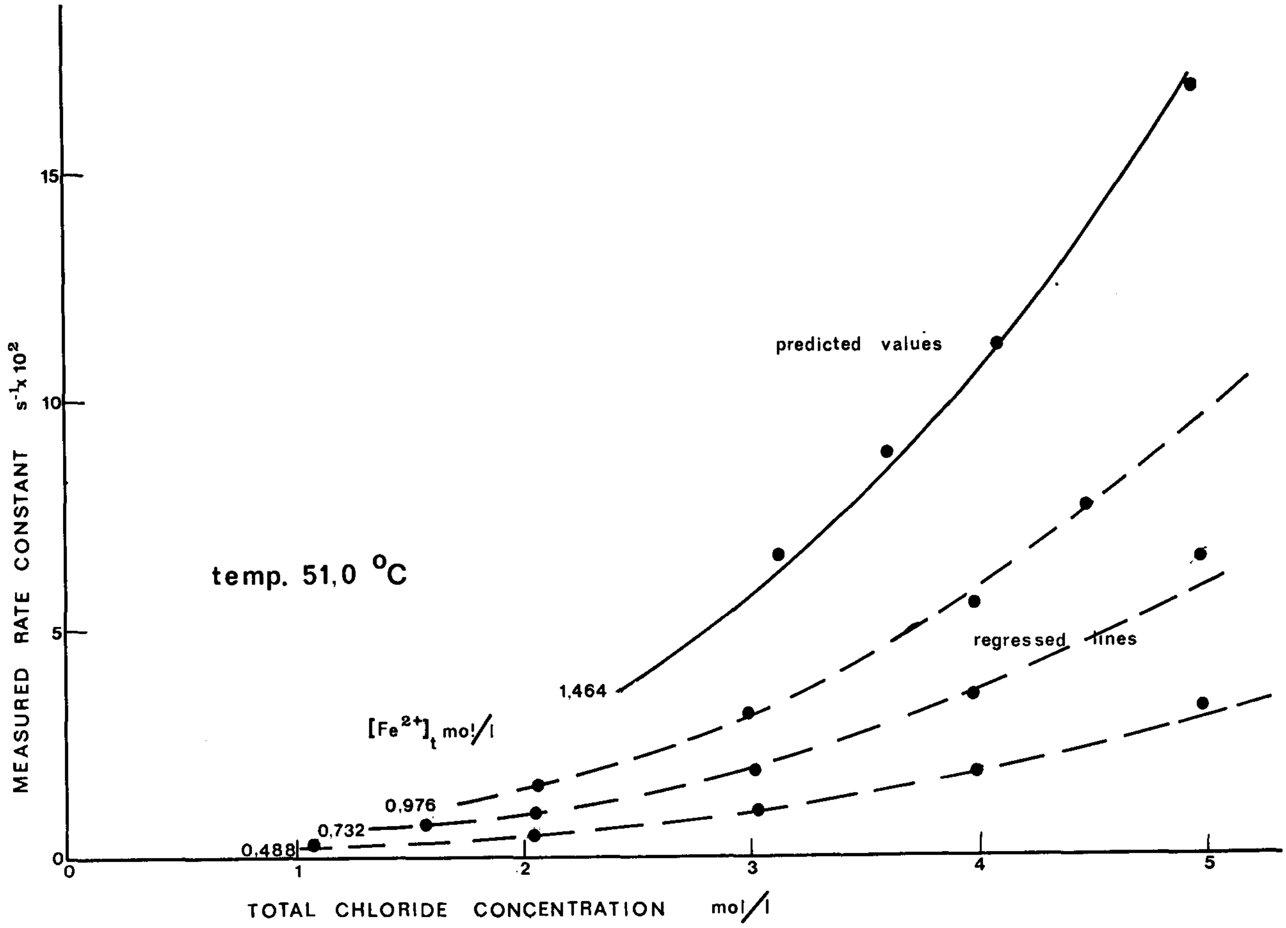

Fig. 4—Regressed and predicted rate constants at 51,0°C as a function of total chloride concentration and ferrous concentration

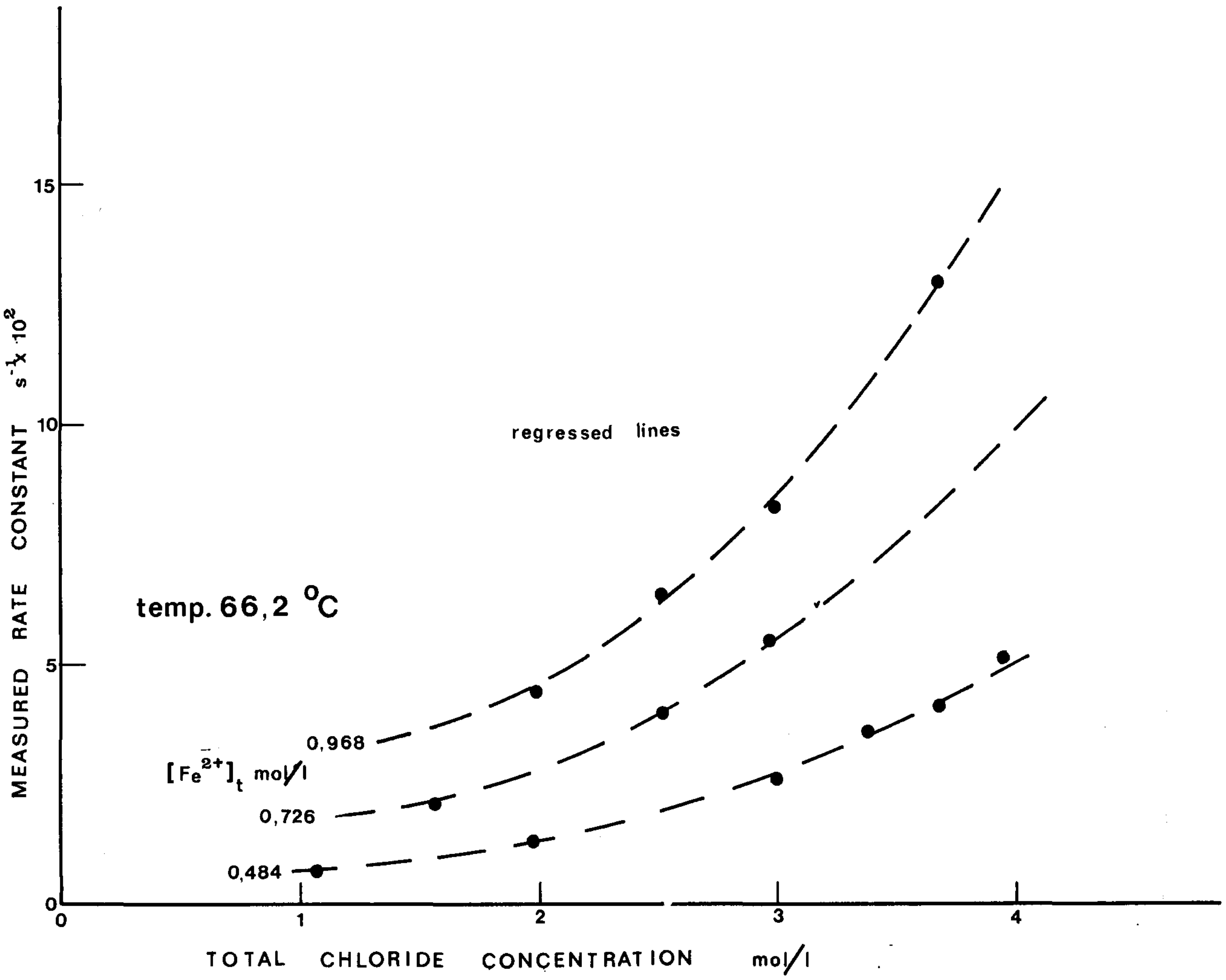

Fig. 5—Regressed rate constants at 66,2°C as a function of total chloride concentration and ferrous concentration

The results obtained for copper are listed in Table VI. Table VII tabulates the results obtained for H^+, Ni^{2+}, Zn^{2+}, NH_4^+, and SO_4^{2-}, and shows that none of the ions has an appreciable effect on the oxidation rate of ferrous chloride. The slight decrease in rate for high concentrations of the NH_4^+ and SO_4^{2-} ions may be ascribed to an increase in the ionic strength.

CONCLUSIONS

The oxidation of ferrous chloride by oxygen is second order with respect to the iron (II) concentration and first order with respect to the oxygen concentration. The dependence on the chloride concentration is complex, but it can be explained by the formation of ferrous chloride complexes, which oxidize more readily than the ferrous ion does. The oxidation rate is also second order with respect to the concentrations of the ferrous chloride complexes.

A kinetic model of the process was developed, and a simplified form of this model adequately described the results obtained; it proved to have satisfactory predictive powers, as shown by Figs. 3, 4 and 5. The values of the activation energies and the frequency factors were determined.

Stability constants for two ferrous chloride complexes were extracted, and the temperature dependence of these constants was determined.

From the results obtained, the oxidation rate of ferrous chloride under any conditions likely to be encountered in hydrometallurgy can be evaluated.

The oxidation rate was shown to be essentially independent of H^+, Zn^{2+}, Ni^{2+}, and SO_4^{2-} concentrations. However, the last three ions were investigated at pH values of 1 only.

The catalytic effect of the cupric ion was very pronounced.

The reasons why copper catalyses, and why the pendence should be as shown, have not been established. A possible mechanism for catalysis by copper could, however, be the following:

$$Cu^{2+}+Fe^{2+} \rightarrow Cu^{+}+Fe^{3+}$$
$$Cu^{+}+O_2 \rightarrow Cu^{2+}+O_2^{-},$$

these reactions occurring in parallel with those considered in the reaction scheme.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Messrs H. K. Streichert and R. Hertel, who conducted the experiments.

This paper is published with the approval of the Director General of the National Institute for Metallurgy, Johannesburg.

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