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Accepted Manuscript

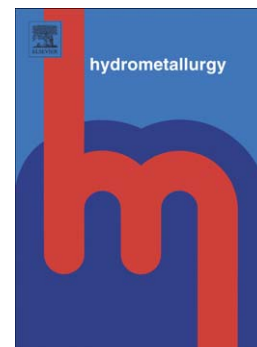
The dissolution of chalcopyrite in chloride solutions. IV. The kinetics of the auto-oxidation of copper(I)

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**The dissolution of chalcopyrite in chloride solutions.
IV. The kinetics of the auto-oxidation of copper(I).**

Hajime Miki ^a, Michael Nicol ^a

^a *Parker Centre, Faculty of Minerals and Energy, Murdoch University, Perth, WA 6150,
Australia*

Abstract

The use of chloride in the heap leaching of sulfide minerals requires the regeneration of the oxidants copper(II) and iron(III). While this is possible in a sulfate system by the use of bacterially catalysed oxidation of iron(II), this can only economically be achieved by chemical reaction with dissolved oxygen in chloride systems due to the sensitivity of bacteria to high concentrations of chloride ions.

The kinetics of the reduction of dissolved oxygen by copper(I) in acidic chloride solutions has been studied under possible heap leach conditions. The results confirm some published data that the rate is second-order in copper(I). The rate increases with increasing acid concentrations but decreases with increasing chloride and copper(II) concentrations. Peroxide has been shown to be a detectable intermediate and a modified mechanism has been proposed which is consistent with the kinetic data. The use of the derived rate equation in a modified rate expression for the copper-catalysed auto-oxidation of iron(II) has been derived.

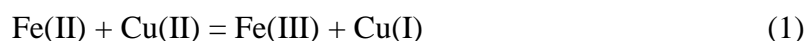
Keywords: copper(I), oxidation, iron(II), kinetics, mechanism, chloride

1. Introduction

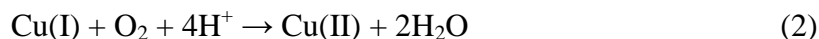
An alternative approach to the heap leaching of primary and secondary copper sulfide minerals involves the use of chloride ions as the lixiviant (Velásquez-Yévenes, Nicol, Miki, 2010). The application of copper(II) as an oxidant and the facile oxidation of copper(I) ions in a chloride system by atmospheric oxygen offers an alternative to bio-oxidation of iron(II) in the sulfate system. In the chloride system, it is well-known that both copper(II) and iron(III) ions can act as the oxidants for these minerals. However, regeneration of these species by oxidation with dissolved oxygen is required and this is possible in a sulfate system by the use of bacterially catalysed oxidation of iron(II). However, in the chloride system, re-oxidation of copper(I) and iron(II) ions can only economically be achieved by chemical reaction with dissolved oxygen.

The kinetics of the reduction of dissolved oxygen by iron(II) and copper(I) in acidic chloride solutions have been previously studied with the former being considerably slower than the latter (Nord, 1955; Nicol, 1983; Moffett and Zika, 1983; Awakura et al., 1986). There is no general agreement on the reaction order with respect to copper(I) with some studies showing first and some second order depending on the concentration of copper(I) used and the presence of copper(II) ions. In addition, only one of these studies (Nicol, 1983) identified the retarding effect of copper(II) ions on the rate.

A previous paper (Miki and Nicol, 2008) focused on the kinetics of the copper-catalysed reaction of iron(II) with dissolved oxygen in acidic chloride solutions. It was shown that this reaction can be described in terms of the rapid equilibrium



coupled to the relatively rapid auto-oxidation of copper(I),



Note that in these and subsequent equations, the use of the generic symbols Cu(I), Cu(II), Fe(II), and Fe(III) are used. This is necessary as each of these species comprises both the aquo-ions and the various chloro-complexes, the relative proportions of which will vary with the chloride ion concentration.

The inhibiting effect of iron(III) ions in terms of the above equilibrium was demonstrated and the effects of the copper(II) concentration, acidity and chloride ion concentration on the rate described. An overall kinetic model was developed which was reasonably consistent with the published data on the individual reactions involved in this mechanism. The application of the model to the prediction of maximum possible leach rates for copper sulfide minerals in aerated systems under ambient conditions was reported.

As part of this mechanism, a previously reported (Nicol, 1983) rate equation for the oxidation of copper(I) by dissolved oxygen in chloride solutions was used. In more recent work on the kinetics of this reaction, it was found that this rate equation is partially inadequate particularly in regard to the effect of copper(II) ions on the rate. This report summarizes additional work as a result of which a slightly modified rate equation for the auto-oxidation of copper(I) is proposed and a more appropriate mechanism for the overall reaction is suggested.

2. Experimental

The kinetics of the oxidation of copper(I) by dissolved oxygen(DO) is too fast to be studied by the previously used technique of monitoring of the DO concentration using a DO probe given the relatively slow response of this system. In an alternative method,

the mass-transport controlled current due to the oxidation of copper(I) at a rotating (1000rpm) platinum disk electrode potentiostatted at 1.0 V (SHE) was followed as a function of time after injection of a small volume of copper(I) solution into a thermostatted, stirred electrochemical cell containing the other reactants saturated with air. The measured limiting current (i) is proportional to the concentration of copper(I) which is the only electroactive species at this potential. Under conditions of low initial concentrations of copper(I), the concentration of dissolved oxygen did not change by more than 10% during an experimental run. Platinum counter and silver/silver chloride reference electrodes were used in a typical 3-electrode system controlled by a PAR 273 Potentiostat.

All reagents were analytical grade. For the regulation of pH, copper and chloride ion concentrations, HCl, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaCl were used respectively. All experiments were conducted at 25°C.

3. Results and Discussion

As shown in the previous paper (Miki and Nicol, 2008), the concentration of copper(I) is small at potentials of about 0.60 V (SHE) which are typically achieved in a chloride heap leach process. From the thermodynamics of the system (Miki and Nicol, 2008), it can be calculated that at a potential of about 0.60 V (SHE), the concentration of copper(I) is about 8 mM for a concentration of 2 gL^{-1} copper(II) and 18 gL^{-1} chloride which could be typical of a heap leach process. For this reason, this study was confined to the use of low concentrations of copper(I).

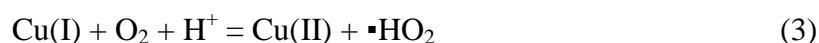
A typical plot of the current due to the oxidation of copper(I) during an experiment is shown in Figure 1. The data is plotted in Figure 2 in terms of the integrated first $f(i) = \ln[(i-i_\infty)/(i_0-i_\infty)]$ or second order $f(i) = 1/(i-i_\infty) - 1/(i_0-i_\infty)$ rate equations in which

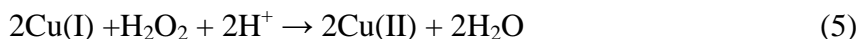
i is the current at any time, t , i_0 is the initial current and i_∞ is the final current. It is apparent that the latter provides a better fit to the data and this was observed in all the runs. Thus, all the data was analysed in terms of the second order rate equation.

Although the second order plots showed good linearity for 60-70% oxidation of copper(I), there were consistent increases in the slopes of the plots at longer times. Furthermore, several consecutive runs in the same aerated solution gave rise to increasing rates and greater deviations from second order. These effects are shown by the plots in Figure 3 for 8 successive runs in the same solution. This observation suggests that there is an accumulation of a reaction product which is also capable of oxidizing copper(I). This species was identified in a previous publication (Nicol, 1983) as being peroxide.

The observed second order rate constants were obtained for a number of experiments in which the initial concentrations of copper(II), chloride ions and acid were varied. The rate decreases with increasing copper(II) concentration as shown by the data in Figure 4 for two chloride ion concentrations at constant acid concentration. The rate increased with increasing acid concentration at fixed copper(II) and total chloride ion concentrations as shown by the data in Figure 5. In the case of the runs at acid concentrations above the total chloride concentration, sulfuric acid was added to increase the acid concentration assuming that only one proton is produced per mole of acid. These data show that the rate constant is proportional to the acid concentration. The rate constant also decreases with increasing chloride concentration at constant acidity and initial copper(II) concentration as shown by the data in Figure 6.

The mechanism previously used was that published (Nicol, 1983) as follows





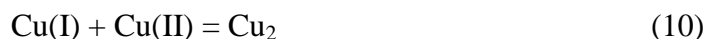
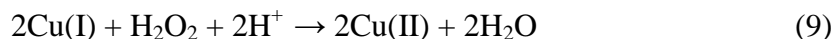
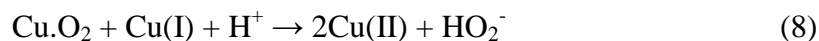
Ignoring any chloride dependence, the rate equation,

$$-\frac{d[\text{Cu(I)}]}{dt} = \frac{k_3 k_4 [\text{H}^+] [\text{Cu(I)}]^2 [\text{O}_2]}{k_4 [\text{Cu(I)}] + k_{-3} [\text{Cu(II)}]} \quad (6)$$

can be derived by assuming that reaction (4) is the slow step and that reaction (3) is a rapid equilibrium and that reaction (5) is rapid.

This equation does roughly describe the kinetic data in that at low concentrations of copper(I) in the presence of added copper(II), it predicts a second order dependence on the copper(I) concentration. However, although it also predicts that the rate should decrease with increasing copper(II) concentration, the dependence of the rate on the copper(II) concentration is not a simple inverse relationship as would be predicted from this rate equation.

An alternative mechanism which is more consistent with the data is suggested as follows



in which copper(I) is oxidised in two parallel reactions, i.e. reactions (7) + (8) by oxygen and reaction (9) by peroxide. The inhibiting effect of copper(II) is ascribed to the formation (reaction 10) of a kinetically inert adduct between copper(I) and

copper(II) ions in chloride solutions, for which there is evidence in the literature (McConnell and Davidson, 1950; Brown et al., 1979). Reaction (9) is comparable in rate to reactions (7) + (8) and therefore peroxide accumulates in the solution giving rise to enhanced rates at long times and after successive runs in the same solution. The effect of complexing of copper(II) and, particularly, copper(I) by chloride ions has not been included in the above mechanism. This mechanism is more plausible given that adducts of dioxygen with copper(I) complexes are well known (Schindler, 2000) and also in that it avoids the formation of the very weakly oxidising superoxide ($\cdot\text{HO}_2$) intermediate.

Assuming that the equilibrium concentration of the intermediate ($\text{Cu}\cdot\text{O}_2$) species is low compared to the total copper(I) concentration, the following rate equation can be derived from this mechanism,

$$-\frac{d[\text{Cu(I)}]}{dt} = \frac{k_8 K_7 [\text{H}^+] [\text{Cu(I)}]^2 [\text{O}_2]}{(1 + K_{10} [\text{Cu(II)}])^2} + k_9 [\text{Cu(I)}] [\text{H}_2\text{O}_2] \quad (11)$$

in which the subscripts refer to the equation numbers above.

The slightly different form of this equation from equation (6) above is apparent in the denominator and in the inclusion of a term for the rate of oxidation of copper(I) by the intermediate peroxide formed which has been found to be first order in both copper(I) and peroxide (Nicol, 1982).

Under conditions of the present experiments, the oxygen concentration is constant in the aerated solution and $[\text{Cu(I)}] \ll [\text{Cu(II)}]$, and, if the initial rate (up to about 60% oxidation of copper(I)) is measured (little accumulated peroxide), this rate equation can be simplified to

$$-\frac{d[\text{Cu(I)}]}{dt} = k_{\text{obs}} [\text{Cu(I)}]^2 \quad (12)$$

with the observed 2nd-order rate constant

$$k_{\text{obs}} = \frac{k_8 K_7 [\text{H}^+][\text{O}_2]}{(1 + K_{10}[\text{Cu(II)}])^2} \quad (13)$$

for $K_{10}[\text{Cu(II)}] < 1$, this expression can be simplified and rearranged to give

$$\frac{[\text{O}_2][\text{H}^+]}{k_{\text{obs}}} = \frac{1}{k_8 K_7} + \frac{2K_{10}}{k_8 K_7} [\text{Cu(II)}] \quad (14)$$

Thus, a plot of $[\text{O}_2][\text{H}^+]/k_{\text{obs}}$ versus $[\text{Cu(II)}]$ should be linear from which the slope and intercept will yield values for $k_8 K_7$ and K_{10} . Such plots are shown in Figure 7 for various chloride concentrations at 25 °C with one set of data also obtained at 15 °C. Constants obtained from the slopes and intercepts of the above lines are summarized in Table 1 for each chloride concentration. It appears that K_{10} is largely independent of the chloride concentration while $k_8 K_7$ is approximately proportional to $[\text{Cl}^-]^{-1.7}$.

The linear dependence of the rate constant on the acid concentration observed in Figure 5 is predicted from equation (13).

The effect of temperature is very small as shown by the data at 15°C in Figure 7 and Table 1, presumably as a result of compensating but opposite effects of temperature on the rate and equilibrium constants of the various steps.

On the basis of the above data at 25 °C, the following rate equation can therefore be used for the initial rates of oxidation of copper(I),

$$-\frac{d[\text{Cu(I)}]}{dt} = k_{\text{obs}} [\text{Cu(I)}]^2 \quad (15)$$

with

$$k_{\text{obs}} = \frac{k [\text{O}_2][\text{H}^+]}{(1 + K_{10}[\text{Cu(II)}])^2 [\text{Cl}^-]^{1.7}} \quad (16)$$

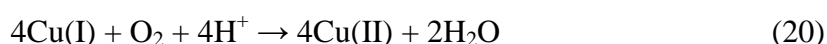
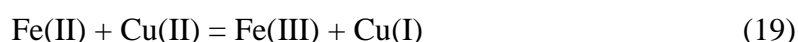
A least squares fit of all the data to this equation at 25 °C gives $k = 7.7 \times 10^6 \text{ M}^{-1.7} \text{ s}^{-1}$ and $K_{10} = 41 \text{ M}^{-1}$. Calculated values of k_{obs} using these parameters are plotted against the observed values in Figure 8 from which it is apparent that the above rate equation provides a reasonable fit to the data.

As described above, the rate of oxidation of copper(I) by the intermediate peroxide is comparable in rate to that of oxidation by dissolved oxygen and the full rate equation (11) should be used. However, given that peroxide is unlikely to accumulate in a real heap leach solution, the second term in the full rate equation has been ignored in the above treatment. Under conditions of constant dissolved oxygen concentration and $[\text{Cu(II)}] \gg [\text{Cu(I)}]$, the full rate equation (11) can be written as

$$-\frac{d[\text{Cu(I)}]}{dt} = k_{\text{obs}}[\text{Cu(I)}]^2 + k_9[\text{Cu(I)}][\text{H}_2\text{O}_2] \quad (17)$$

The data for a run with 0.25 gL^{-1} copper(II) in 0.2 M HCl has been fitted to the above rate equation using a modified Euler Predictor method and the result shown in Figure 9 from which it is apparent that peroxide accumulates during the reaction. The best-fit value for $k_9 = 500 \text{ M}^{-1}\text{s}^{-1}$ obtained in this case can be compared with published values of $270 \text{ M}^{-1}\text{s}^{-1}$ in 0.2 M HCl (Nicol, 1982), $260 \text{ M}^{-1}\text{s}^{-1}$ in 2 M HCl (Skinner et al., 1980) and $58 \text{ M}^{-1}\text{s}^{-1}$ in 1M HCl (Kolthoff and Woods, 1966). Given the relative insensitivity of the fit on the choice of k_9 and the instability of peroxide, the agreement is reasonable.

As outlined in a previous publication (Miki and Nicol, 2008), the simplest interpretation of the observed catalysis by copper ions and inhibition by ferric ions in the auto-oxidation of ferrous irons in chloride solutions is in terms of the following mechanism



in which iron(II) is oxidised in two parallel reactions, the second of which (reactions (19) plus (20)) is the copper-catalysed reaction. As shown above, reaction (20) is composed of two successive reactions involving peroxide as an intermediate.

Thus, the catalytic effect of copper ions and the retarding effect of ferric ions on the rate can be explained in terms of the effect of these ions on the steady state concentration of copper(I) established through the assumed equilibrium step (Eq. 19).

On the basis of these rate determining steps, one can write

$$-\frac{d[\text{Fe(II)}]}{dt} = k_7[\text{Fe(II)}]^2[\text{O}_2] + \frac{k[\text{Cu(I)}]^2[\text{O}_2]}{(1 + K_{10}[\text{Cu(II)}])^2} \quad (21)$$

The first term is the published rate expression for reaction (18) (Nicol and Colburn, 1973) and the second a simplified version of that derived above in which the effects of peroxide, chloride and acidity have been ignored.

The rate of reaction (19) is rapid relative to reaction (18) or (20) and can be assumed to be in equilibrium (Orth and Liddell, 1990). Substitution of $[\text{Cu(I)}] = K_{19}[\text{Fe(II)}][\text{Cu(II)}]/[\text{Fe(III)}]$ in this equation gives

$$-\frac{d[\text{Fe(II)}]}{dt} = -\frac{4d[\text{O}_2]}{dt} = k_7[\text{Fe(II)}]^2[\text{O}_2] + \frac{k K_{19}^2[\text{Fe(II)}]^2[\text{Cu(II)}]^2[\text{O}_2]}{[\text{Fe(III)}]^2(1 + K_{10}[\text{Cu(II)}])^2} \quad (22)$$

In the presence of copper ions and low iron(III) concentrations, reactions (18) + (20) are faster than reaction (18) and the overall rate equation can be written as

$$-d[\text{Fe(II)}]/dt = \frac{k K_{19}^2 [\text{Fe(II)}]^2 [\text{Cu(II)}]^2 [\text{O}_2]}{[\text{Fe(III)}]^2 (1 + K_{10}[\text{Cu(II)}])^2} \quad (23)$$

Note that k and K_{19} are functions of the acidity and chloride concentration. Examination of this equation shows that the rate should increase with increasing copper(II) concentration but should become independent of the copper(II) concentration at high concentrations of copper(II). Data provided in the previous publication (Miki and Nicol, 2008) is reproduced in Figure 10 which supports this prediction.

4. Conclusions

A revised rate equation and mechanism for the oxidation of copper(I) ions in chloride solutions has been established based on additional testwork using a different technique for the study of the kinetics at low concentrations of copper(I) typical of those encountered in a heap leach process. Formation of peroxide as an intermediate in the reduction of oxygen has been confirmed and a preliminary analysis has shown that the rate constant derived from the data for one experiment is consistent with published data.

The modified rate equation has been incorporated into a revised overall rate equation for the copper-catalysed auto-oxidation of iron(II) in chloride solutions. This revised

rate equation more accurately describe the retarding effect of copper(II) concentration on the rate of this reaction. It is recommended that the modified rate equation be used in any kinetic modeling of a chloride heap leach process.

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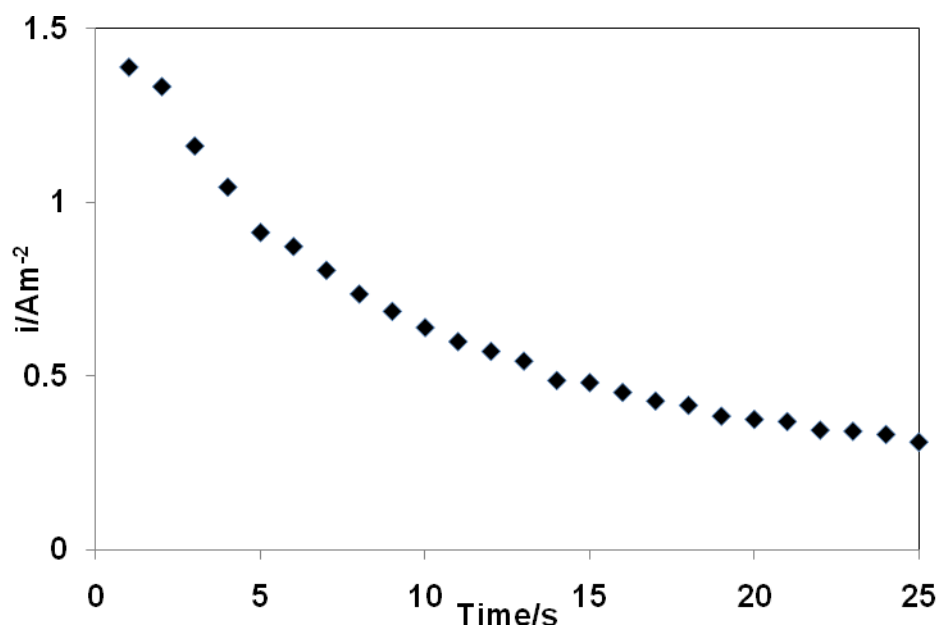
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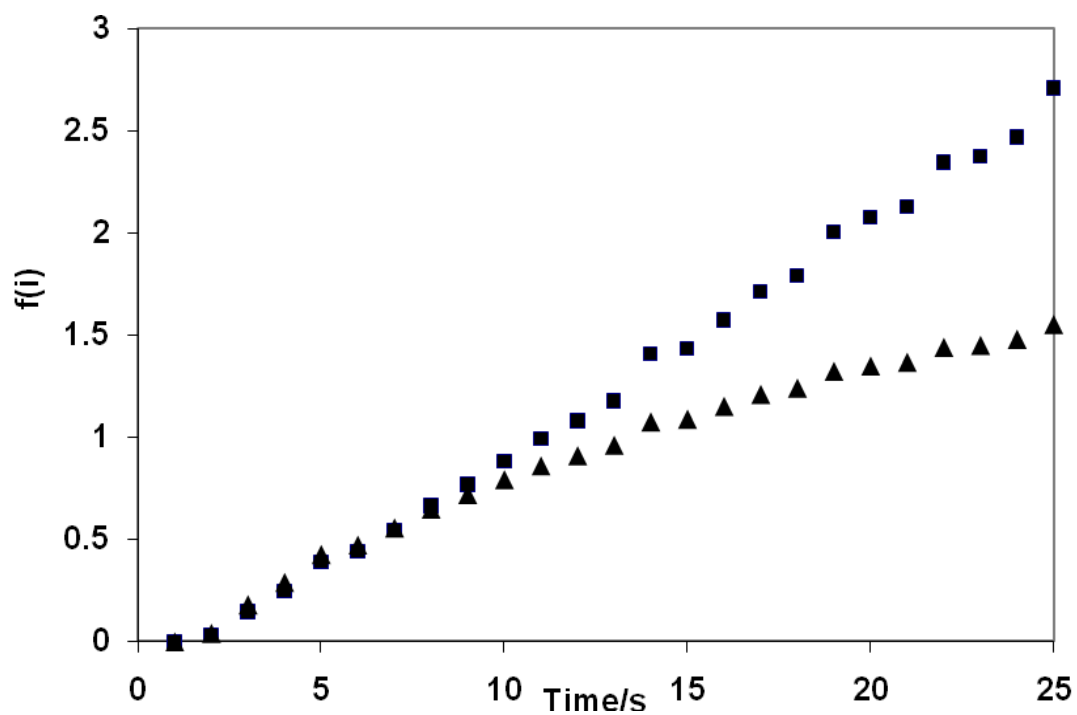
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Figure 1. Current due to oxidation of copper(I) (8×10^{-5} M) during oxidation by dissolved oxygen in a solution containing 0.25 gL^{-1} copper(II) and 0.2 M HCl at $25 \text{ }^\circ\text{C}$.



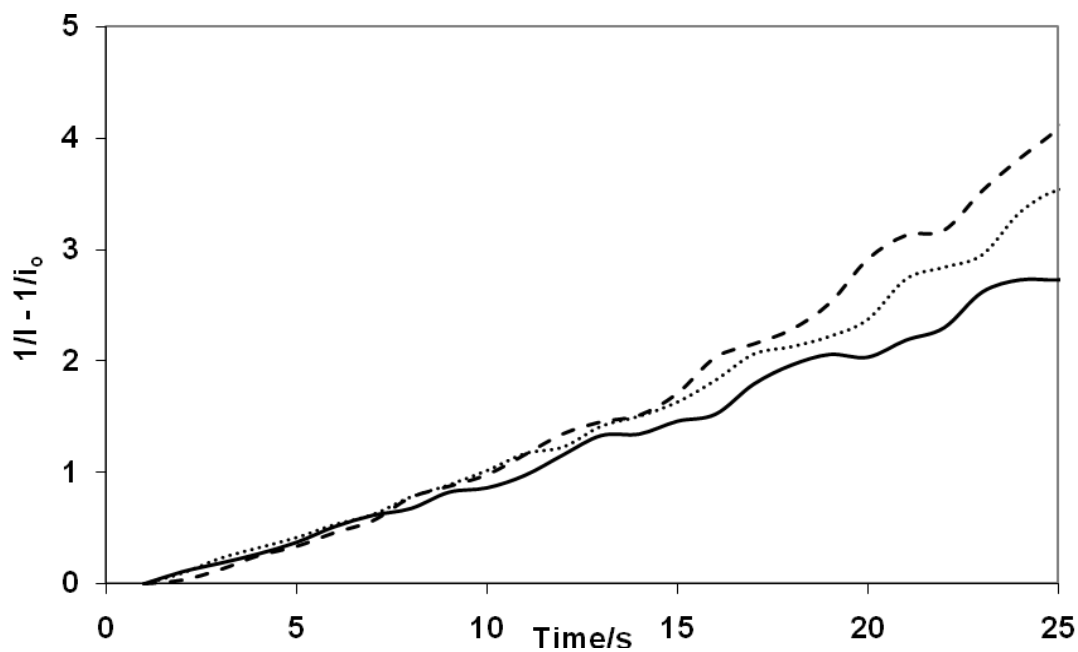
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Figure 2. Plots of the data from Figure 1 for the rate of oxidation of copper(I) according to (\blacktriangle) 1st order, (\blacksquare) 2nd order reaction.



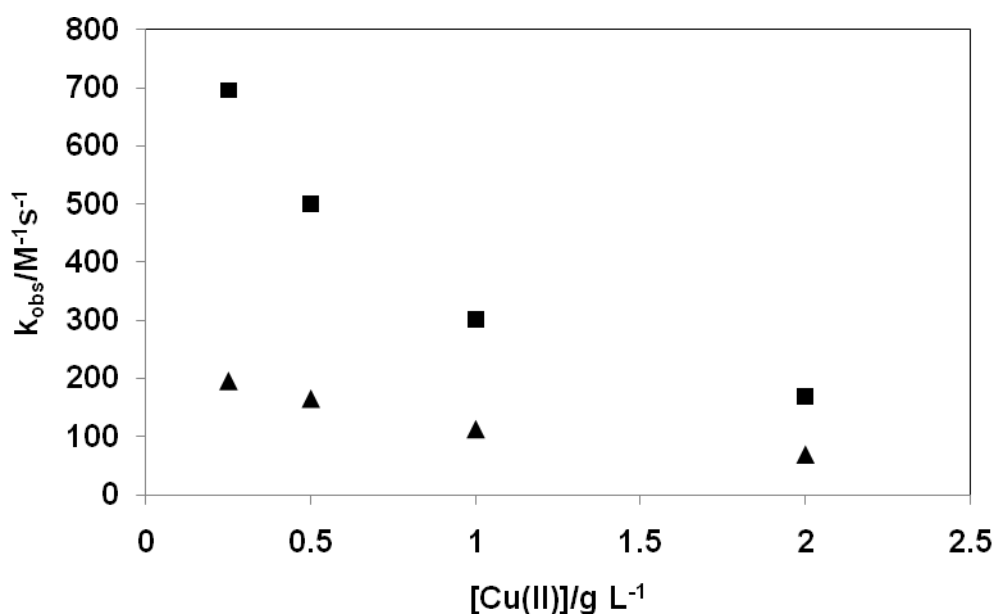
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Figure 3. 2nd order plots for the oxidation of copper(I) in a solution containing 0.5 gL⁻¹ copper(II) and 0.2 M HCl at 25 °C. Successive runs were carried out in the same solution by injection of aliquots of copper(I) to give an initial concentration of 8 x 10⁻⁵ M for each run. (—) 1st run, (.....) 4th run, (----) 8th run.



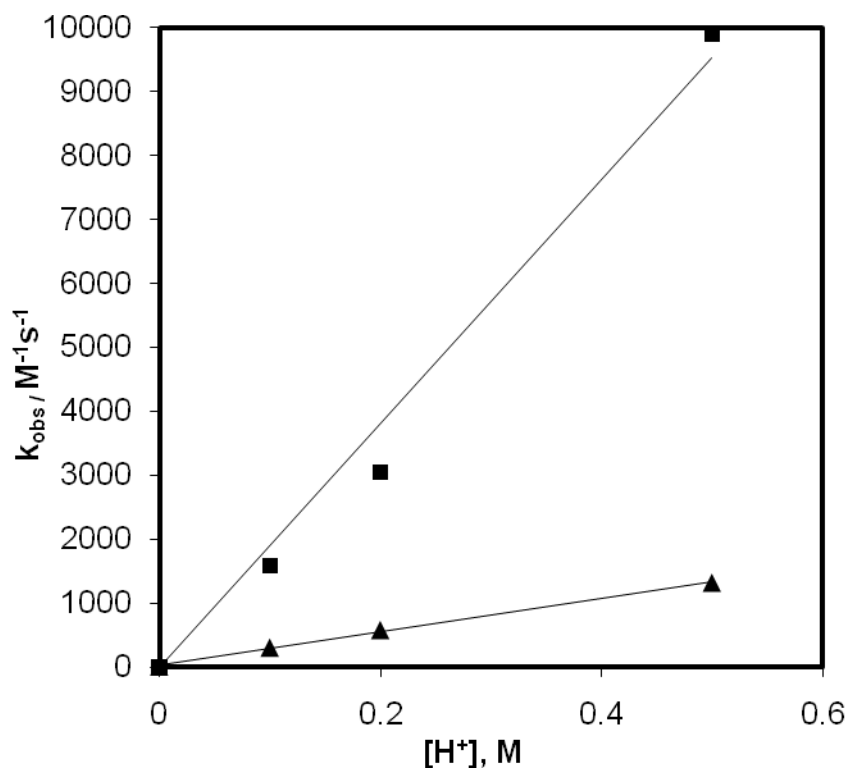
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Figure 4. Effect of copper(II) concentration on the second order rate constants in solutions containing 0.2 M HCl and (▲) 1M total chloride, (■) 0.5M total chloride at 25 °C.



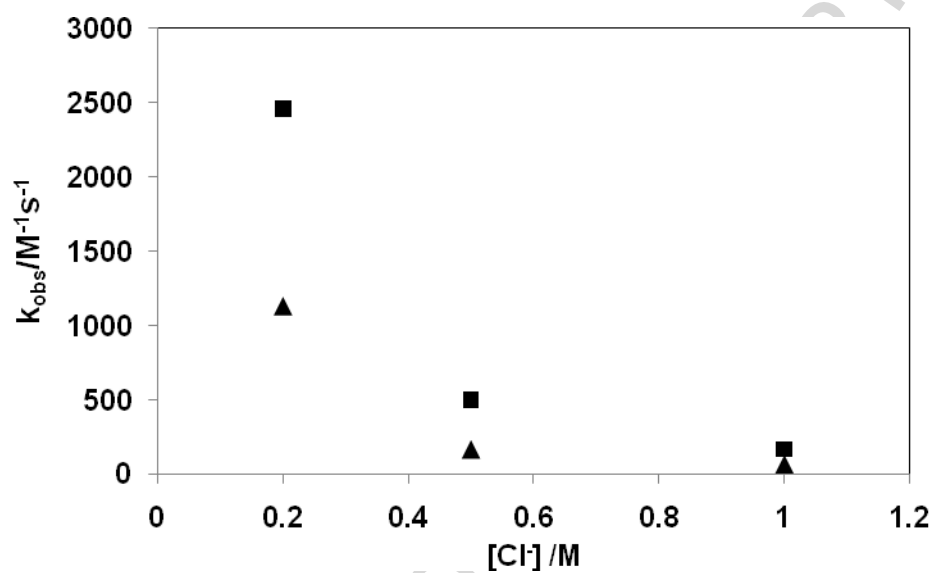
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Figure 5. Effect of acid concentration on the second order rate constants in solutions containing 0.5 gL^{-1} copper(II) and (■) 0.2 M total chloride, (▲) 0.5 M total chloride at $25 \text{ }^\circ\text{C}$.



ACQ

Figure 6. Effect of chloride concentration on the second order rate constants in solutions containing 0.2 M HCl and (\blacktriangle) 2 g L⁻¹ copper(II), (\blacksquare) 0.5 g L⁻¹ copper(II) at 25 °C.



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Figure 7. Plots of the data according to equation 8. (●) 0.2 M chloride, 25 °C, (▲) 0.5 M chloride, 25 °C, (Δ) 0.5 M chloride, 15 °C, (◆) 1.0 M chloride, 25 °C.

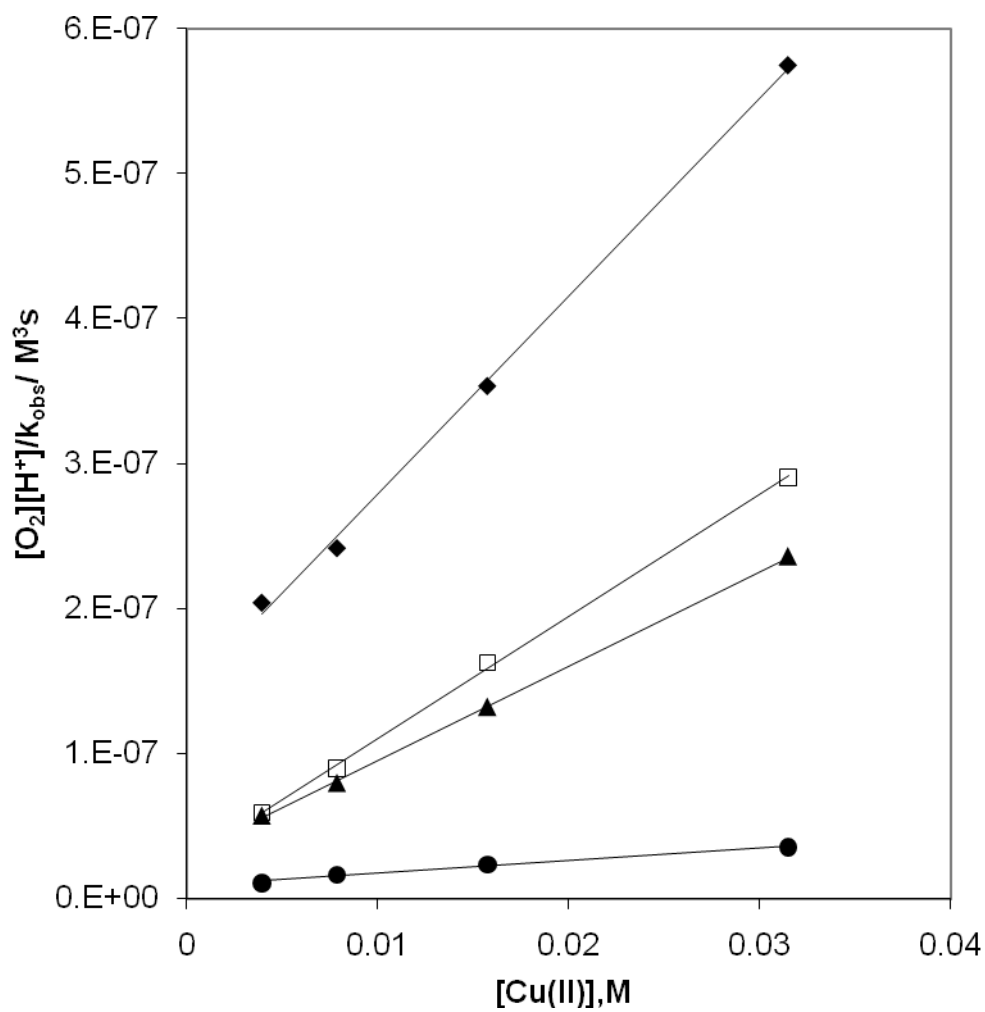


Figure 8. Comparison of observed and calculated values of the 2nd-order rate constant for various concentrations of chloride, acid and copper(II) at 25 °C.

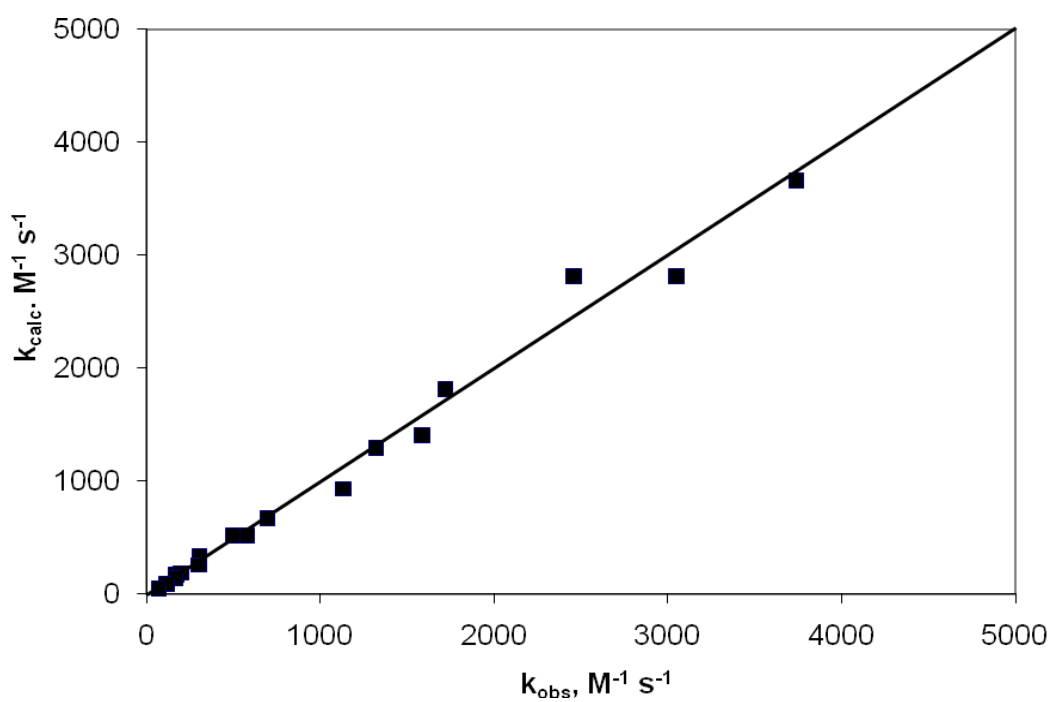
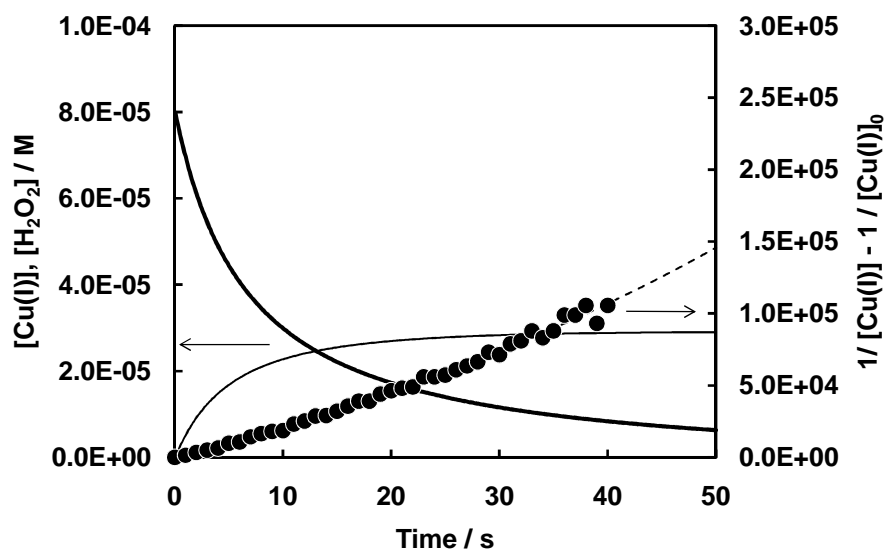
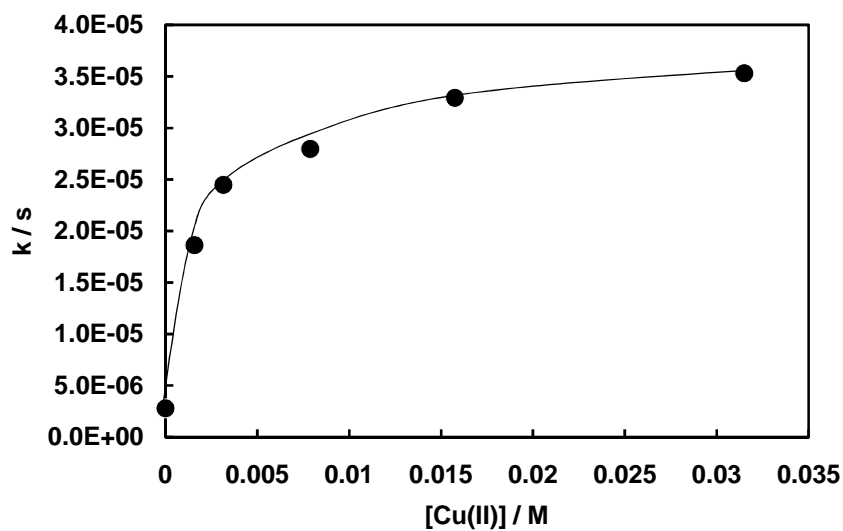


Figure 9. Comparison of observed and calculated concentrations and 2nd-order plots for the oxidation of copper(I) in a solution of 0.25 gL⁻¹ copper(II) and 0.2 M HCl. (—) calculated copper(I) concentration, (—) calculated H₂O₂ concentration, (---) calculated value of $1/[\text{Cu(I)}] - 1/[\text{Cu(I)}]_0$, (●) measured value of $1/[\text{Cu(I)}] - 1/[\text{Cu(I)}]_0$.



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Figure 10. Effect of copper(II) concentration on the rate of reduction of dissolved oxygen by iron(II) in a solution of 0.2 M HCl, 0.22 M NaCl, 0.1 M iron(II), 0.01 M iron(III) at 25 °C (from Miki et al., 2008).



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Table 1. Constants derived from the plots in Figure 7.

[Cl]	k_8K_7	K_{10}
M	$M^{-3}s^{-1}$	M^{-1}
0.2	1.16×10^8	51
0.5	2.91×10^7	87
1	7.03×10^6	48
0.5 (15°C)	3.82×10^7	161

Research Highlights

- Auto-oxidation of copper(I) second order in copper(I)
- Rate first order in acid concentration
- Rate decreases with increasing copper(II) and chloride
- Revised mechanism proposed.

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