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Date October 12th, 2001
ABSTRACT

The influence of gas-liquid reactions on oxygen mass transfer in three hydrometallurgical leaching systems under typical operating conditions has been investigated and assessed in terms of enhancement factors and Hatta numbers. The gas-liquid reactions considered were: Fe(II) oxidation under zinc pressure leaching conditions, Cu(I) oxidation in sulphate media under conditions used for the total oxidation of copper sulphides, and Cu(I) oxidation in ammoniacal media under conditions used for ammonia leaching of copper sulphides.

Mass transfer rates and interfacial areas were determined simultaneously in order to obtain the parameters necessary for the evaluation of the enhancement factors. Performing oxygen absorption tests via surface aeration under a flat interface with a single impeller situated at the bottom of the stirrer shaft rotating at moderate speeds fulfilled this requirement. An attempt was also made to determine directly the gas-liquid reaction rate constant for Hatta number calculations in tests carried out in a well-agitated reactor fitted with dual impellers. The progress of Fe(II) oxidation was followed by sampling and titration, whereas the progress of Cu(I) oxidation was followed by measuring the rate of oxygen consumption using gas mass flowmeters. Reactant concentrations in the two copper systems were estimated using a speciation routine based on the minimization of Gibbs free energy. Density and viscosity of all solutions were also measured at low temperatures, and extrapolated to elevated temperatures using available correlations and curve fitting.

Hatta numbers obtained from Fe(II) oxidation tests under a flat interface were greater than 3, situating the reaction in the very fast regime. However, similar values evaluated from tests carried out in a well-agitated reactor fell between 0.3 and 3, categorizing the reaction in the intermediate regime.
An instantaneous reaction model in the two copper systems successfully modeled experimental results from well-agitated reactor tests. Results of speciation calculations indicate that metallic copper existed prior to the introduction of oxygen when the metallic copper charge exceeded 5 g/L in sulphate media. However, all of the metallic copper was converted to Cu(I) in ammoniacal media. Enhancement factors estimated from flat interface data indicated that the reactions in the two systems fall under the very fast reaction regime, complementing the well-agitated reactor test results.

Based on the results, it is concluded that oxygen mass transfer rates may be determined using the gas-liquid reactions typically taking place in certain hydrometallurgical systems. The Hatta numbers and enhancement factors obtained indicate that all solutions are depleted of oxygen at the high concentrations of Fe(II) and Cu(I) in both sulphate and ammoniacal media, and therefore, the use of oxygen solubility in solving the kinetic equations appears to be suspect. The nature of the gas-liquid interface (stagnant film versus surface renewal) has a notable effect on both the kinetics of Fe(II) oxidation and oxygen mass transfer. In the two Cu(I) systems, oxygen mass transfer is enhanced several times over the maximum possible rate of physical absorption under the same conditions. Finally, with some modifications it would be possible to evaluate mass transfer parameters directly from the rate of Cu(I) oxidation in either sulphate or ammoniacal media.

It is recommended that, whenever possible, Hatta numbers or enhancement factors be evaluated for all gas-liquid reactions and incorporated into the design of hydrometallurgical reactors. Further studies are recommended to determine the solubility of ferrous sulphate under zinc pressure leaching conditions, the bulk concentration of oxygen under test conditions, and oxygen solubility in solutions containing Fe(II).
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NOMENCLATURE

A  gaseous reactant, oxygen

\( A \)  a parameter in equation (3-2) for viscosity estimation at elevated temperature, [-]

\( a \)  specific interfacial area, \([m^2/m^3]\)

\( a_j \)  activity of species \( j \), [-]

B  reactant solute

\( B \)  a parameter in equation (3-2) for viscosity estimation at elevated temperature, [-]

\( C_A, C_A^0 \)  dissolved gas concentration in the bulk solution, \([kmol/m^3]\)

\( C_A^*, C_A^i \)  dissolved gas concentration in equilibrium with gas at a given pressure (gas solubility), \([kmol/m^3]\)

\( C_A^*,w \)  gas solubility in pure water, \([kmol/m^3]\)

\( C_B, C_B^0 \)  reactant solute concentration in the bulk solution, \([kmol/m^3]\)

\( C_B^* \)  the maximum possible concentration of Cu(I) or Cu(NH\(_3\))\(_2^+\) if all the metallic copper were initially completely converted to Cu(I) or Cu(NH\(_3\))\(_2^+\), \([kmol/m^3]\)

\( C_i \)  concentration of species \( i \), \([kmol/m^3]\)

\( C_p \)  heat capacity, \([kJ/kg-K]\)

\( D_A \)  dissolved gas diffusivity, \([m^2/s]\)

\( D_A-w \)  dissolved gas diffusivity in pure water, \([m^2/s]\)

\( D_l \)  impeller diameter, m

\( E \)  enhancement factor, [-]

\( E_a \)  activation energy, \([kJ/kmol-K]\)
$E_i$ enhancement factor for an instantaneous reaction, [-]
$f$ mass fraction of solution consisting of dissolved solutes, [-]
$g$ gravitational acceleration, [9.81 m/s$^2$]
$\Delta G^\circ_j$ standard Gibbs free energy of species $j$, [kJ/mol]
$\Delta G_k$ Gibbs free energy of reaction $k$, [kJ/mol]
$h$ heat transfer coefficient, [W/m-K]
$H$ Henrian coefficient, [Pa]
$h_i$ salting out parameter for electrolyte species $i$, [m$^3$/kmol]
$Ha$ Hatta number, [-]
$Ha^*$ Hatta number based on the maximum possible Cu[II] or Cu(NH$_3$)$_2$$^+$ concentration, $C_B^*$, [-]
$I$ ionic strength, [kmol/m$^3$]
$k_2$ second order reaction rate constant, [m$^3$kmol$^{-1}$s$^{-1}$]
$k$ intrinsic reaction rate constant, [$k_{mn}C_B$]
$k_G$ gas side mass transfer coefficient, [m/s]
$K_G$ overall mass transfer coefficient referring to the gas film, [m/s]
$k_L$ liquid side mass transfer coefficient, [m/s]
$K_L$ overall mass transfer coefficient referring to the liquid film, [m/s]
$k_{La}$ volumetric liquid side mass transfer coefficient, [s$^{-1}$]
$k_{La,w}$ liquid side mass transfer coefficient in pure water, [m/s]
$k_{mn}$ rate constant for reaction $m$th order in A and $n$th order in B, [(m$^3$/kmol)$^{m+n-1}$ s$^{-1}$]
$K_{Se}$ Sechenov constant or salting out coefficient, [m$^3$/kmol]
\( K_2 \) second dissociation constant for sulphuric acid, \([\text{kmol/m}^3]\)

\( m \) order of reaction with respect to the gaseous solute, [-]

\( m_A^* \) molal gas solubility, \([\text{mol/kg H}_2\text{O}]\)

\( m_A^{*,\text{w}} \) molal gas solubility in pure water, \([\text{mol/kg H}_2\text{O}]\)

\( m_i \) molal concentration of species \( i \), \([\text{mol/kg water}]\)

\( M_i \) molecular weight of species \( i \), \([\text{kg/kmol}]\)

\( n \) order of reaction with respect to the reactant solute, [-]

\( N_{cr} \) critical impeller rotation speed, \([\text{s}^{-1}]\)

\( p \) gas pressure, \([\text{kPa}]\)

\( p_a \) atmospheric pressure, \([\text{kPa}]\)

\( p_A \) partial pressure of \( A \) in equilibrium with the liquid at the gas liquid interface, \([\text{kPa}]\)

\( Pr \) Prandtl number, [-]

\( q \) exponent in equations 2-54 and 2-55, [-]

\( R \) rate of mass transfer, \([\text{kmol/s}]\); universal gas constant, \([8.314 \text{ kJ/kmol-K}]\)

\( s \) rate of surface renewal, \([\text{s}^{-1}]\)

\( S \) oxygen solubility in zinc pressure leaching solution, \([\text{g/L}]\)

\( Sc \) Schmidt number, [-]

\( T \) temperature, \([\text{K}]\)

\( T_{cr} \) absolute critical temperature, \([\text{K}]\)

\( t \) duration of exposure, \([\text{s}]\)

\( X_B \) fraction of \( B \) unreacted based on \( C_B^* \), [-]
\( x_A \)  mole fraction gas solubility, [-]

\( y \) exponent in equation 2-53, [-]

\( z \) number of moles of B reacting with one mole of A, [-]

\( Z_i \) valency of ionic species \( i \), [-]

\( Z_D \) concentration-diffusion parameter

**Greek letters**

\( a_{ij} \) number of atoms \( i \) in species \( j \), [-]

\( \beta \) liquid holdup, [-]

\( \gamma \) the ratio \( \frac{D_g}{zD_A} \), [-]

\( \gamma_j \) activity coefficient of species \( j \), [-]

\( \delta_l \) liquid film thickness for physical gas absorption, [m]

\( \delta_r \) liquid film thickness for gas absorption accompanied by chemical reaction, [m]

\( \varepsilon_i \) empirical constant in equation 2-35, [-]

\( \eta \) exponent in equation 2-53, [-]

\( \kappa \) coefficient in equation 2-53, [-]

\( \lambda \) Lagrange’s unspecified multiplier, [-]

\( \mu \) viscosity, [Pa-s]

\( \mu_w \) viscosity of pure water, [Pa-s]

\( \nu_{jk} \) stoichiometric factor of species \( j \) in reaction \( k \), [-]

\( \rho \) density, [kg/m\(^3\)]
\( \rho_w \)  
density of pure water, [kg/m\(^3\)]

\( \sigma \)  
the ratio \( \frac{Y_{C^*}}{C^*_A} \), [-]

\( \varphi \)  
water fraction in electrolyte solution available for absorbing oxygen, [-]

\( \varphi_{\text{eff}} \)  
effective \( \varphi \) in a solution containing several electrolytes, [-]

\( \varphi_i \)  
value of \( \varphi \) for the \( i \)th solute in a solution of mixed electrolytes, [-]

\( \psi \)  
fraction of reactant B that is converted, [-]

\( \omega_i \)  
empirical constant in equation 2-36, [-]
CHAPTER 1

INTRODUCTION

In the presence of a gas-liquid chemical reaction, the absorption of a gas from the gas phase into a solution is considered to take place through two sequential steps. The first step is the dissolution of the gas into the solution at the gas-liquid interface, followed by the diffusion of the dissolved gas through the solution boundary layer accompanied by the chemical reaction. Diffusion accompanied with chemical reaction controls the overall rate of absorption. The absorbed gas may react with either a solute reactant dissolved in the solution or with the solvent. It is known that the rate of gas absorption accompanied by chemical reaction can be much higher than simple physical absorption (Astarita, 1967). Oxygen is often used as a reactant in several hydrometallurgical processes. The use of oxygen in the oxidative pressure leaching of sulphide mineral concentrates presents a situation where the reaction between oxygen and reactants derived from the minerals can influence the rate of oxygen absorption into the leaching solutions.

In sulphuric acid oxidative pressure leaching of zinc sulphide or ammonia leaching of copper sulphide, the direct reaction between molecular oxygen and sulphide minerals is not significant (Chalkley and Weir, 1983; Peters, 1987). Normally, the oxygen first oxidizes a reducing agent such as ferrous or cuprous ion, producing a “surrogate” oxidant, which then does the oxidative work at the mineral surface. Therefore, the actual gas-liquid reactions in these oxidative leaching systems involve the oxidation of reducing agents to produce surrogate oxidants. It is now evident that during zinc pressure leaching, for instance, the oxidative leach reactions are too fast to be supported by oxygen mass transfer based on a simple mechanism of physical absorption of oxygen gas (Peters, 1987). Similarly, the oxygen mass transfer in the oxidative ammonia leach of copper sulphides has been found to
be faster than a simple physical absorption of oxygen would predict. In both
cases, oxygen mass transfer is intensified by the chemical reaction between
oxygen and the reducing agent. No study in the literature has dealt with
oxygen mass transfer in oxidative sulphate leaching of copper sulphide
concentrates.

The influence of a liquid phase chemical reaction which accompanies a
gas absorption process is commonly assessed in chemical engineering theory
by the use of the enhancement factor (Shaikh, 1994) and the Hatta number
(Charpentier, 1981). The fundamental knowledge on the various types and
regimes of gas-liquid reactions is well-established (Charpentier, 1985;
Levenspiel and Godfrey, 1974). However, information concerning the types
and regimes of the reactions between oxygen and ferrous ions in zinc
pressure leaching or cuprous ions in ammonia or sulphate leaching of copper
sulphides is lacking. In addition, gas-liquid reactions at elevated temperature
and pressure have not been given adequate attention in the literature, even
though a number of important gas-liquid reactions of industrial interest take
place under these conditions (Suresh et al., 1988b). While tremendous
advances have been made in developing gas-liquid reaction models
(Charpentier, 1981; Danckwerts, 1970) similar advances are lacking in
gathering the basic physico-chemical data for these systems (Katti, 1995).

The kinetic mechanisms for the oxidation of ferrous ions (Dreisinger and
Peters, 1989; Dreisinger et al., 1990; Iwai et al., 1982; Chmielewski and
Cherewicz, 1984; Awakura et al., 1986) and the oxidative ammonia leaching
of copper sulphide (Beckstead and Miller, 1978; Kuhn et al., 1974; Reilly and
Scott, 1976; Williams and Light, 1978) have been studied extensively.
However, bearing in mind the way in which these hydrometallurgical
processes operate, the reactions should be studied as gas-liquid reactions in
which both mass transfer and reaction kinetics have a role to play. None of
the studies cited above took this approach; instead only the kinetics of the
reactions were considered. Simultaneous studies of kinetics and mass
transfer can be accomplished by using the Hatta number and the enhancement factors. The Hatta number accounts for both mass transfer and the chemical gas-liquid reaction. In this study Hatta numbers were evaluated at various conditions relevant for three pressure leaching systems, namely, ferrous oxidation under zinc pressure leaching conditions, Cu(I) oxidation under conditions used for sulphate leaching of copper sulphides and Cu(I) oxidation under conditions for ammonia leaching of copper or nickel sulphides.

Many investigators who have studied oxygen mass transfer have done so by modeling the hydrometallurgical systems without considering the influence of the chemical reactions involved on oxygen mass transfer. In this kind of model, the oxygen is considered to be physically absorbed into the leaching solutions. The absorbed oxygen is then assumed to react with the aqueous reactant or mineral particle in the bulk solution. Such studies have treated the absorption of oxygen in hydrometallurgical reactors totally as physical absorption and the effect the chemical reactions between the absorbed oxygen and reactants found in these systems is completely ignored. Therefore, many are interested in the value of the volumetric mass transfer coefficient, $k_L a$, without any consideration for the possibility that the coefficient could be enhanced significantly by the chemical reaction. This avenue has not been studied thoroughly despite the existence of several cases of absorption accompanied by a chemical reaction that are of practical importance in hydrometallurgical systems.

The sulphite oxidation reaction has been almost exclusively applied for the purpose of determining $k_L a$ at conditions of low catalyst concentration where the enhancement factor equals one. However, gas-liquid processes in hydrometallurgy may involve rate-controlling steps different from those of the sulphite system. Furthermore, the sulphite system could not be used under certain conditions of interest to hydrometallurgy such as low pH (pH of application is $7.5 < \text{pH} < 9$), in other concentrated electrolyte solutions or
even at high temperature where its applicability has not been well established. For example, the recommended temperature for the determination of interfacial area ranges from 15 to less than 60°C (Cieszkowski and Dylag, 1994). Additionally, the sulphite oxidation reaction is very sensitive to the presence of impurities. Ethyl alcohol, amines and manitol inhibit the reaction whereas Na$_2$CO$_3$, Sn(OH)$_4$, Fe(OH)$_2$ and NaOH were found to retard the reaction (Linek and Vacek, 1981). Besides copper and cobalt, the sulphite oxidation reaction can also be accelerated by other metal ions such as Fe$^{2+}$ and Mn$^{2+}$. The reaction has often been used at low temperatures up to 35°C (Linek and Vacek, 1981; Amoah, 1991), occasionally at moderately high temperatures up to about 70°C (Cheng, 1994) and rarely at higher temperatures up to 240°C (Foussard et al., 1984).

The main objective of the present work was to determine how actual gas-liquid chemical reactions taking place under typical hydrometallurgical process conditions influence the rate of oxygen absorption. This was achieved by establishing the reaction regime for each of the gas-liquid reactions considered. Second, the aim was to assess the suitability of using the gas-liquid reactions occurring in three hydrometallurgical processes for the determination of mass transfer parameters. These reactions are ferrous oxidation under zinc pressure leaching conditions, cuprous oxidation under conditions of total sulphate oxidation of copper sulphides and the oxidation of cuprous amines under conditions of ammonia leaching of copper sulphides.
CHAPTER 2

MASS TRANSFER IN GAS-LIQUID SYSTEMS

In gas-liquid systems mass transfer can take place during a physical absorption of gases in liquids or when there is a chemical reaction between the absorbed gas and the absorbing liquid or a solute dissolved in the liquid. The design of gas-liquid equipment is, therefore, determined by two major considerations. First, the distribution of components between phases in a state of thermodynamic equilibrium defined as gas solubility in liquids. Second, the rate at which mass transfer occurs under prevailing conditions as dictated by diffusivity and the rate of chemical reaction. For this reason, physico-chemical parameters and interfacial parameters for specified hydrodynamic working regimes are always required. The theories governing mass transfer in both cases have been well presented in the published literature (Astarita, 1967; Charpentier, 1981; Danckwerts, 1970; Hatta, 1929, 1931, 1932). These are reviewed and discussed below.

2.1 PHYSICAL ABSORPTION

The rate of physical mass transfer, where a gas dissolves in a liquid without reacting, is best represented by the double-film theory (Whitman, 1923; Lewis and Whitman, 1924) as,

\[ R = k_G a (p_A - p_A^*) = k_L a (C_A^* - C_A^b) \]

Eq. 2-1

For systems obeying Henry's law for equilibrium at the interface \((p_A^* = HC_A^*)\) the additivity of the film resistances may be expressed as follows:

\[ \frac{1}{K_L} = \frac{1}{k_L} + \frac{H}{k_G} = \frac{H}{K_G} \]

Eq. 2-2

where \(H\) is the Henry's law constant and \(K_G\) and \(K_L\) are the overall mass transfer coefficients referring to the gas and liquid films respectively. For a
very soluble gas, $H$ is very large, gas film resistance becomes controlling and therefore the resistance expression reduces to:

$$K_G \approx k_G$$  \hspace{1cm} \text{Eq. 2-3}

The gas phase mass transfer coefficient is usually high leading to negligible gas phase resistance (Calderbank, 1959). If the gas is sparingly soluble, $H$ is very small and the resistance to mass transfer is almost entirely in the liquid film, which can be estimated by the expression:

$$K_L \approx k_L$$  \hspace{1cm} \text{Eq. 2-4}

The resistance encountered by the diffusing molecules is due to their collision with interfering molecules of the gas or liquid through which diffusion takes place. The collisions in the liquid phase are much more frequent and the corresponding resistance is greater than in gas.

The solubility of oxygen in hydrometallurgical systems is so low that the gas side mass transfer coefficient can be neglected. Indeed, the gas-side mass transfer coefficient for a pure oxygen system and an air system were found to be equal (Yoshida et al., 1960). This result means that the gas phase oxygen mass transfer resistance is negligible compared to that in the liquid phase. Hence, in gas-liquid hydrometallurgical mass transfer systems involving oxygen as the gaseous solute the liquid side mass transfer coefficient ($k_L$) is the major parameter of concern. The assumption of a liquid phase mass transfer controlled process is entirely appropriate since oxygen is a sparingly soluble gas in water and aqueous solutions, and hence, essentially all of the resistance to mass transfer resides in the liquid phase. For example, studies have confirmed that the gas-liquid mass transfer of sparingly soluble gases in water is predominantly liquid phase mass transfer controlled (Treybal, 1980).

There are three distinct hypotheses about the behaviour of the liquid boundary layer leading to different expressions for the liquid-side mass transfer coefficient. The Film model assumes that even in a fully developed
turbulent flow a stagnant film or laminar flow boundary film of thickness $\delta_L$ develops near the gas-liquid interface. The film is considered to be stationary and so thin that steady state diffusion and equilibrium between gas and liquid at the interface are established immediately. The film also contains all the resistance to mass transfer found in the liquid. The mass transfer in this case is given by the expression:

$$k_L = \frac{D_A}{\delta_L} \quad \text{Eq. 2-5}$$

The direct use of such an expression is rendered difficult, however, by the need to predict the fictitious film thickness $\delta_L$. The penetration and surface renewal models are based on the assumption that there is an identifiable finite mass of fluid that is transported from the bulk to the interface. This fluid mass spends a relatively short time at the interface with respect to the time required to saturate the fluid mass with gas. The fluid mass then transfers back to the bulk without transferring mass on the way and instantly mixes back into the bulk liquid. The surface renewal model provides two more expressions for $k_L$. Higbie (1935) assumed that every element of the surface is exposed for the same duration $t$ before being replaced by liquid from the bulk solution, thus:

$$k_L = 2\left(\frac{D_A}{\pi t}\right)^{1/2} \quad \text{Eq. 2-6}$$

The use of this expression requires an estimation of a rest time $t$ for the mass of fluid as it sits at the interface.

Under the supposition of Danckwerts (1951) that the probability of a surface element of the interface being replaced by a fresh eddy from the bulk solution is independent of the length of time for which it has been exposed, the expression becomes:

$$k_L = 2(D_A s)^{1/2} \quad \text{Eq. 2-7}$$
where $s$ is the surface renewal rate.

Direct use of this equation is hampered by the difficulty in estimating the rate of surface renewal ($s$). The film thickness $\delta_L$ accounts for the hydrodynamic properties of the system in the film model and depends on geometry, physical properties and agitation intensity. Similarly, the contact time $t$ and the surface renewal frequency $s$ represent hydrodynamic properties in the Higbie and Danckwerts models, respectively.

These theoretical models of absorption lead to conclusions that are numerically similar whether the film model or a surface renewal model is used as the basis of calculation (Danckwerts, 1970). In many circumstances, the differences between predictions made on the basis of these models are less than the uncertainties about the value of physical quantities such as the diffusion coefficient or the gas solubility used in the calculation (Charpentier, 1978). Therefore, the three models can be regarded as interchangeable for many practical purposes and it is merely a question of conviction or convenience which one is found in practice to lead to accurate predictions or to a simplified expression. For example, the film model has been used because of its mathematical simplicity for predicting and analyzing the effects of such additional complicating factors to mass transfer as simultaneous chemical reaction near the interface.

Experiments have shown that for a gas-liquid system of specified physical properties, the mass transfer coefficient varies relatively little with the degree and type of agitation (Midoux and Charpentier, 1984). Therefore, the only sure way to accelerate or retard the rate of mass transfer is by changing the surface area. According to the data of Calderbank and Moo-Young (1961) the liquid phase mass transfer coefficient may be assumed to be practically independent of operating conditions such as gas flowrate, bubble diameter and mixing intensity. This was again substantiated by the findings of Hyman (1962), who reported that the mass transfer coefficient is relatively constant even at high rates of shear. The rate of gas absorption per
unit area does not increase indefinitely but tends to a maximum (Becker, 1924). The plot of rates of absorption against the stirring speed resulted in a straight line, indicating that mass transfer per unit time varies linearly with the stirring rate. However, when the effect of variation in area produced by the stirring was taken into account, the plot of the rates per unit interfacial area resulted in a curve. The two behaviours are illustrated in Figure 2-1.

Mass transfer rate per unit area is equal to the mass transfer coefficient multiplied by the concentration difference available as the driving force and is given as:

$$\frac{R}{a} = k_L(C_A^* - C_A^b)$$  \hspace{1cm} \text{Eq. 2-8}

On the other hand, the mass transfer coefficient is the ratio of the flux to the concentration (or composition) difference and can be represented by:

$$k_L = \frac{R}{a(C_A^* - C_A^b)}$$  \hspace{1cm} \text{Eq. 2-9}

The gas solubility $C_A^*$ does not change with stirring speed. If the bulk liquid gas concentration $C_A^b$ is kept constant (= 0 for initial absorption rates in gas-free liquids) the only variable that can vary with the rate of stirring would be the mass transfer coefficient. The approach of the mass transfer per unit area to a maximum value is further evidence that the mass transfer coefficient remains relatively constant after a certain agitation speed is attained.
Figure 2-1  Variation of mass transfer coefficient with stirrer speed and interfacial area (data from Becker, 1962)
2.2 MASS TRANSFER WITH CHEMICAL REACTION

Many of the gas-liquid systems of hydrometallurgical interest involve gas absorption accompanied by a chemical reaction. The main purpose of gas liquid mixing in these cases, therefore, is to supply a gaseous reagent to be used in a chemical reaction after it dissolves or as it dissolves. If the chemical reaction is slow, the reaction takes place in the bulk of the solution after gas dissolution. If it is fast, however, most or all of the reaction may occur in the liquid film surrounding the gas-liquid interface as the gas dissolves.

When a gas dissolving in a liquid is involved in a chemical reaction it dissolves faster than in a pure physical dissolution of the gas at the same driving force. It is to be suspected that the concentration profile of the gas in the vicinity of the gas-liquid interface is being modified by the chemical reaction. Although a chemical reaction has no effect on the interfacial area, slow reactions are known to reduce the concentration of the gaseous solute in the bulk solution, while fast reactions deplete completely the gaseous solute in the bulk solution, giving a larger driving force for mass transfer. Furthermore, the mass transfer coefficient increases with the rate of reaction accompanying the absorption of a reactive gas into solution. In other words, and assuming the film model, the gas-liquid chemical reaction produces an effective reaction layer of thickness $\delta_r$ that is less than the diffusion layer thickness for physical absorption $\delta_L$. This effect is conveniently presented in terms of an enhancement or reaction factor, $E$ and the Hatta number, $Ha$ (Bravo et al., 1996; Shaikh, 1994; Katii, 1995; Charpentier, 1981). Both terms relate the rate of mass transfer accompanied by a chemical reaction to that of purely physical absorption.

2.2.1 Enhancement factor

The liquid phase mass transfer coefficient is strongly influenced by fast chemical reactions and generally increases with increasing reaction rate. The
gas phase mass transfer coefficient $k_G$ is not affected by the fact that a chemical reaction takes place only in the liquid phase. In most cases, although the reaction consumes the solute gas as it dissolves, hence enhancing both the mass transfer coefficient and the driving force for absorption, the reaction rate is sufficiently slow that the liquid phase resistance must be taken into account. This may be due to either an insufficient supply of the second reagent or to an inherently slow chemical reaction.

In any case the value of the liquid-phase mass transfer coefficient in the presence of a chemical reaction is normally larger than the value found when only physical gas absorption takes place. This fact has led to the presentation of the effect of chemical reaction in terms of a reaction factor or enhancement factor. The enhancement factor is the ratio of the amount of gas absorbed within a given time into a reactive liquid, or a solution containing a reactive solute, to the amount that would be absorbed if there was no chemical reaction. It is evaluated when the concentration of the gaseous solute in the bulk solution is zero in both cases. The factor is defined by the expression:

$$E = \frac{R}{k_l a C_A^{b}}$$

Eq. 2-10

Thus, the mass transfer coefficient with chemical reaction is the product of the coefficient for physical absorption based on the maximum driving force for physical absorption (i.e. $C_A^{b} = 0$) and the chemical enhancement factor, $E$. $R$ here stands for the rate of mass transfer when the absorbed gas is involved in a chemical reaction.

### 2.2.2 Hatta number

The Hatta number is the ratio of the rate of homogeneous reaction relative to the rate of gas dissolution, and is therefore a measure of the contribution of chemical reaction to mass transfer. The Hatta number is also a measure of the amount of dissolved gas that reacts in the diffusion film near
the gas-liquid interface compared to that which reaches the bulk of the solution in the unreacted state. When this quantity is zero we have a purely physical absorption in which case the dissolved gas diffuses from the interface to the bulk without reacting along the way. The higher the value of the Hatta number, the stronger is the effect of chemical reaction on mass transfer.

In the film model, the square of the Hatta number, also known as the film conversion parameter, is defined as the ratio of the maximum possible conversion in the film to the maximum rate of diffusive transport through the film:

\[
Ha^2 = \frac{\text{maximum possible conversion in film}}{\text{maximum diffusion transport through film}}
\]

This value is used to tell whether the reaction is slow, fast or intermediate. If the conversion parameter is much greater than 1 \((Ha^2 >> 1)\), all reaction occurs within the film and the gas-liquid interfacial area is the controlling factor. On the other hand, if the conversion parameter is much less than 1 \((Ha^2 << 1)\), no reaction occurs within the film, and the bulk volume controls the rate. In this case there is no benefit from an increase in interfacial area. Therefore, the Hatta number is actually the criterion for determining whether the reaction occurs more or less completely in the bulk of the liquid. When \(Ha < 0.02\), contact devices that have high liquid holdup are necessary. For reactions taking place in both the bulk and the film, both a large volume of liquid and a large interfacial area are required, whereas reactions occurring in the film when \(Ha > 3\) necessitate a large interfacial area.

For a general case of binary reaction between a dissolved gas “A” and a single solute “B” of order \(m\) in the gaseous solute A and order \(n\) in solute B, the rate of the chemical reaction is equal to \(k_{mn}C_A^mC_B^n\). The Hatta number is then given by:
2.2.2.1 Hatta number regimes

The value of the Hatta number gives several regimes of interest in the choice of gas-liquid reactors. These are defined depending on the rate of the gas reaction in the liquid. For the purpose of analysis, all gas-liquid reactions are categorized into four Hatta number regimes. Representative liquid phase concentration profiles for the different regimes are presented in Figure 2-2. Unless otherwise specified, reactions where the dissolved gas undergoes an irreversible second order reaction with a reactant B dissolved in the liquid will be considered in reviewing the Hatta number regimes.

For a second order gas-liquid chemical reaction of stoichiometry represented by the reaction \(\text{A} + z\text{B} \rightarrow \text{products}\), the rate equations can be written as:
\[
\begin{align*}
    r_A &= k_2C_AC_B \\
    r_B &= zr_A
\end{align*}
\]  

Eq. 2-13

When the conditions in the film achieve steady state, the two equations for material balance are:
\[
\begin{align*}
    D_A \left( \frac{d^2C_A}{dx^2} \right) - k_2C_AC_B &= 0 \\
    D_B \left( \frac{d^2C_B}{dx^2} \right) - zk_2C_AC_B &= 0
\end{align*}
\]

Eq. 2-14

Eq. 2-15

In these expressions \(x\) is the distance in the liquid from the gas-liquid interface and \(D_A\) and \(D_B\) are the diffusion coefficients of reactants A and B in the liquid, respectively.
Figure 2-2  Liquid-phase concentration profiles for mass transfer with chemical reaction: film theory (Charpentier, 1981)
At the gas-liquid interface the boundary conditions are:

\[ C_A = C_A^* \text{ at } x = 0 \]  \hspace{1cm} \text{Eq. 2-16}

\[ \frac{dC_B}{dx} = 0 \text{ at } x = 0 \]  \hspace{1cm} \text{Eq. 2-17}

The boundary condition for component B at the inner edge of the liquid-film (where \( x = \delta_L \)) is:

\[ C_B = C_B^b \text{ at } x = \delta_L \]  \hspace{1cm} \text{Eq. 2-18}

In a gas-liquid reaction some of the gaseous component reacts within the film while some may be transferred across the film to react in the bulk of the liquid. The boundary condition in such a case for the gaseous component thus becomes:

\[ -D_A \left( \frac{dC_A}{dx} \right)_{x=\delta_L} = k_z C_A^b C_B^b \left( \frac{\beta}{a} - \delta_L \right) \]  \hspace{1cm} \text{Eq. 2-19}

where \( a \) is the specific interfacial area, \( \beta \) is the liquid holdup, and the volume of the bulk of liquid is \( \left( \frac{\beta}{a} - \delta_L \right) \). Representative concentration profiles are depicted in Figure 2-2.

A complete analytical solution of equation 2-14 and 2-15 is not possible. However, numerical and analytical solutions can be evaluated for part of the range of variables. The solutions are expressed in terms of the enhancement factor, \( E \). A graphical plot of the complete solution of the equations is presented in Figure 2-3. In this figure the enhancement factor \( E \) is plotted as a function of the Hatta number.
Figure 2-3 Enhancement factor plotted against the Hatta number for a second order gas-liquid reaction (Charpentier, 1981)
Figure 2-4  Enhancement factor for second order reaction for Hatta numbers greater than 3 (Ha > 3) (Charpentier, 1981)
Very slow reaction in the bulk liquid: $Ha < 0.02$

In this case virtually no reaction takes place in the liquid film and mass transfer is used to keep the bulk concentration of the gas in the liquid close to its saturation value. Sufficient interfacial area is a necessary requirement. However, high liquid holdup is more important and the use of a bubble column would be suitable. For a second order reaction the governing equation is:

$$R = k_L a (C_A^* - C_A^b) = kC_A^bC_B^b \beta$$ \hspace{1cm} \text{Eq. 2-20}

where $\beta$ is the fraction of liquid in the gas-liquid mixture, also known as liquid holdup and hence

$$C_A^b = \frac{C_A^*}{1 + \left( \frac{\beta kC_B^b}{k_L a} \right)}$$ \hspace{1cm} \text{Eq. 2-21}

When the chemical reaction rate is very small and $C_A^b$ approaches $C_A^*$ the rate of the whole process is completely determined by the rate of the chemical reaction in the bulk liquid.

Slow reaction in bulk liquid: $0.02 < Ha < 0.3$

In this regime, an appreciable amount of the absorbed gas reacts in the bulk liquid. However, a negligible proportion of absorbed gas reacts in the diffusive film. The process here starts with an almost physical absorption and is followed by a chemical reaction in the bulk liquid. If the reaction is sufficiently fast to hold $C_A^b$ close to zero and the enhancement factor $E = 1$ then:

$$R = k_L a C_A^*$$ \hspace{1cm} \text{Eq. 2-22}

For this situation, both interfacial area and liquid holdup should be high and the use of a mechanically agitated tank would be suitable. The rate of the
process is completely determined by mass transfer across the liquid film and is proportional to \( k_L a \). This result is the basis for using chemical reactions to measure \( k_L a \) directly from the rate of absorption when \( C_A^* \) is known. The well-known application of the sulphite oxidation method in the presence of cobalt or copper catalyst to obtain \( k_L a \) falls in this category.

**Moderately Fast Reaction: \( 0.3 < Ha < 3 \)**

In this region, the reaction is fast enough for a substantial amount of dissolved gas to react within the gas-liquid film. The concentration of the dissolved gas in the bulk liquid is very low. If the enhancement factor \( E \) is appreciably greater than 1, the reaction has an appreciable effect on the rate of absorption. In the two preceding cases, only a small amount of the gaseous reactant A is consumed by the reaction in the liquid film and the gas concentration was estimated by a linear profile. Unlike those two, however, the concentration profile here is curved and is steeper at the gas-liquid interface. Hence, the rate of mass transfer of the absorbed gas is enhanced. The enhancement factor is the ratio of the concentration gradient at the gas-liquid interface \( j-j \), to the concentration gradient at the inner edge of the film \( i-i \) as indicated in Figure 2-2 (c). Due to the fast chemical reaction \( C_A^b \) is very low and if \( E \) is appreciably higher than 1 the reaction has a significant effect on the rate of gas absorption. The effect is governed by Equation 2-10. Here, the interfacial area begins to outweigh the volume of the bulk liquid in controlling the total reaction rate.

**Fast reaction in the diffusive film: \( Ha > 3 \)**

This is the case where the reaction is fast and takes place virtually completely in the liquid film as the gas is being absorbed. The concentration of the gas in the bulk liquid is virtually nil. For such reactions, the rate of absorption is directly proportional to the interfacial area. Therefore, a high interfacial area is required in the reactor. However, the liquid holdup is not
important and for homogeneous reactions the use of a packed column or plate column would be suitable. For an irreversible \((m,n)\)-th order reaction, with a rate given by \( r = k_{mn}C_A^mC_B^n \), the relationship between the enhancement factor \( E \), the Hatta number \( \text{Ha} \), and the instantaneous reaction enhancement factor \( E_i \) is approximated (Hakita and Asai, 1964) as:

\[
E = \frac{\text{Ha} \left( \frac{E_i - E}{E_i - 1} \right)^{n/2}}{\tanh \left( \text{Ha} \left( \frac{E_i - E}{E_i - 1} \right)^{n/2} \right)}
\]

**Eq. 2-23**

In this relationship, \( E_i \) is the enhancement factor for an instantaneous reaction and is given by the equation:

\[
E_i = 1 + \left( \frac{D_B}{zD_A} \right) \left( \frac{C_B}{C_A} \right)
\]

**Eq. 2-24**

According to Hakita and Asai (1964) the value of the ratio \( D_B/D_A \) for most practical cases lies between 4 and 0.25. Most researchers have used the ratio 1 (Danckwerts, 1970) which is the intermediate value for the practical range of the diffusivity ratio.

The relationship between the Hatta number and the enhancement factor is depicted in Figure 2-4. Two limiting types of behaviour can be derived from this regime.

*Fast pseudo-mth-order: \( 3 < \text{Ha} < E_i/2 \)*

When the concentration of reactant B is much higher than that of A, reactant B has a negligible variation throughout the liquid phase and the reaction is pseudo-\(m\)th order with a reaction rate constant:

\[
k = k_{mn}(C_B^b)^n
\]

**Eq. 2-25**

When \( 3 < \text{Ha} < E_i \), the dissolved gas reacts in the diffusion film and none diffuses into the bulk. The enhancement factor is approximately equal to the
Hatta number and the average rate of absorption is independent of the film thickness or the mass transfer coefficient $k_L$. This rate can be approximated by the expression:

$$R = E k_L a C_A^* = H a \cdot k_L a C_A^*$$  \hspace{1cm} \text{Eq. 2-26}$$

Substituting the overall expression for the Hatta number from Equation 2-12 we obtain:

$$R = a \sqrt{\frac{2}{m+1} D_A k_m (C_A^*)^{m+1} (C_B^*)^n}$$  \hspace{1cm} \text{Eq. 2-27}$$

This case is the basis for measuring the interfacial area directly from the rate of absorption of gas into a reactive solution. Also the reaction rate constant can be obtained for a known interfacial area. In fact this is the only equation that can be used to determine the reaction rate constant for very fast reactions because the concentration of the gaseous solute in the bulk liquid is zero. The concentration profile is as presented in Figure 2-2 (e). Therefore, the kinetic equation $r = k(C_A^{b})^m(C_B^{b})^n$ cannot be evaluated.

\textbf{Instantaneous reaction: $Ha > 10 E_1$}

An increase in the Hatta number leads to a limiting value when $E = E_i$. This condition can result when the reaction constant is high, the concentration of reactant B is substantially less than the gas solubility, or the physical mass transfer rate is low. The dissolved gas reacts instantaneously with reactant B. The concentration of both components then becomes zero at a certain distance away from the interface. The concentration profile for a reaction falling under this regime resembles that shown in Figure 2-2 (f). The rate of reaction is equal to the rate at which the two components can diffuse to the reaction plane. The actual kinetics of the reaction is no longer important. The reactant B is depleted in the neighbourhood of the interface to the extent that the rate of the reaction is determined by diffusion alone. The rate can be estimated by the equation:
\[ R = E_i k_{i} a C^*_A \]  \hspace{1cm} \text{Eq. 2-28}

It should be noted that all reactions have finite reaction rates and the concept of 'instantaneous' is relative. A high specific reaction rate of dissolved gas, combined with a low diffusion coefficient of (physical) absorption promotes quasi-instantaneous behaviour.

2.2.2.2 **Hatta number for surface renewal models**

Similar relationships between the enhancement factor and the Hatta number for the film model may be applied with Higbie's surface renewal model. The Hatta number expression must be replaced by the equation:

\[ Ha' = \sqrt{\frac{\pi}{4} k C_{b}^{b} t} \]  \hspace{1cm} \text{Eq. 2-29}

Similarly, the instantaneous enhancement factor expression must be replaced by the equation:

\[ E_i' = E_i \left( \frac{D_A}{D_b} \right)^{1/2} \]  \hspace{1cm} \text{Eq. 2-30}

The Hatta number expression based on the Higbie model is difficult to use for stirred reactors, which are the most common reactors in hydrometallurgy, because unlike other types of reactors the exposure time, \( t \) is not known and is difficult to estimate. However, the expression for the enhancement factor is the same as that obtained with the film model when \( D_A = D_B \).

The Danckwerts model is less amenable to a simple analysis except where the reaction is pseudo-first order based on the gaseous component, A.

A conclusion of practical importance is that, although the expressions for the three models look very different, they give the same enhancement factor values to within a few percent for values of the Hatta number between 0.1 and \( \infty \).
2.2.2.3 Summary on Hatta number regimes

Since the value of the Hatta number is an important indication of whether a large specific area or a large liquid hold-up is required for a particular gas-liquid reaction with a given rate constant, the Hatta number has to be considered when choosing the appropriate type of gas-liquid reactor.

The Hatta number regimes can be summarized as follows: For slow reactions the mass transfer from gas to liquid is not limiting and the size of the reactor depends almost exclusively on the requirements of conversion. This is the case when the Hatta number is less than 0.3. With faster reactions, the mass transfer rate, besides the reaction kinetics, is the determining factor for the overall process. This is when the value of the Hatta number is between 0.3 and 3. For very fast reactions, when the Hatta number is larger than 3, the mass transfer rate is the sole determining factor and a chemically enhanced mass transfer will take place. This means that the reaction will mainly take place near the gas-liquid interface.

2.2.3 Effect of variables on the Hatta number

From the theory of Hatta number one may expect that oxygen absorption in aqueous hydrometallurgical solutions containing reducing agents such as cuprous ions and ferrous ions can be very fast depending on the prevailing conditions. Also, under oxidative leaching conditions, temperature, solution composition and the presence of other additives could substantially influence the Hatta number. To comprehend the influence of these variables on the Hatta number, oxygen mass transfer data were obtained at typical operating conditions, and temperature was an important variable in this study. Many important gas-liquid reactions in hydrometallurgy are carried out in continuous stirred autoclaves over a wide range of temperature in which a continuous shift from chemical reaction to mass transfer control can occur.
From the Hatta number expression in Equation 2-12, Hatta number is expected to increase as the mass transfer coefficient $k_L$ decreases and the reaction rate constant $k$ increases. Also, an increase in the bulk concentration of the solute $C_B$ will result in a higher Hatta number. In order to understand the impact of these variables on the Hatta number, the influence of each variable defining the Hatta number will now be examined.

### 2.2.3.1 Mass transfer coefficient $k_L$

Due to the difficulties of measuring mass transfer coefficients directly, volumetric mass transfer coefficients $k_La$ are normally reported in the literature instead. The value $k_L$ is then obtained indirectly from the volumetric mass transfer coefficient by determining the interfacial area of the gas-liquid system considered. Therefore, in order to understand the effect of temperature on the mass transfer coefficient, it is necessary first to consider the effect of temperature on the volumetric mass transfer coefficient and the interfacial area.

The effect of temperature on the volumetric mass transfer coefficient $k_La$ may be explained mainly by variations in the liquid phase viscosity and diffusion coefficient with temperature (Whitney and Vivian, 1949).

It is important to recognize that the effects of temperature on the liquid phase diffusion coefficients and viscosity can be very large and therefore must be carefully accounted for when using $k_L$. Temperature affects the physical properties of both gas and liquid phases and should affect gas liquid mass transfer coefficients and interfacial area. Raising the temperature typically causes reductions in solution viscosity, surface tension and liquid density. High temperatures also increase gas diffusivity (Bird et al., 1960).

Liquid density is responsible for the inertial forces on the gas bubbles, which cause the bubble diameters to decrease. A decrease in the density favours increased bubble diameters and hence a reduction in the specific interfacial area. Surface tension forces cause increases in the rates of
coalescence and bubble growth. Reducing surface tension as a result of raising temperature aids the formation of small bubbles, which in turn increase the specific interfacial area. Coalescence of gas bubbles is diminished if the liquid viscosity increases. High temperatures tend to decrease viscosity thus promoting the coalescence of small bubbles into larger ones resulting in reduced interfacial area. The mass transfer coefficient $k_L$ is proportional to the gas diffusivity $D_A$. An increase in gas diffusivity leads to a corresponding increase in the value of $k_L$. Furthermore, the equation of Calderbank and Moo-Young (1961) gives for large bubbles (with size > 2 mm diameter):

$$k_L = 0.42 \left( \frac{\mu_L g}{\rho_L} \right)^{1/3} = 0.42 \left( \frac{D_A \rho_L g^2}{\mu_L} \right)^{1/6}$$

**Eq. 2-31**

where $Sc$ is the Schmidt number. This equation is the result of the correlation of data obtained at 25°C and atmospheric pressure and is applicable in mixing vessels as well as in turbulent fluids flowing through fixed beds and pipes. The equation indicates that $k_L$ is a function of the viscosity and density of the liquid as well as the diffusivity of the solute gas through the liquid. Thus, the overall effect of temperature on $k_La$ depends on the competition between the effects of the temperature on $k_L$ and on interfacial area.

This might be one reason, among others, for the failure of researchers to come up with a common effect of temperature on $k_La$. The effect reported in literature for $k_La$ values seems not to follow any particular trend. Some researchers found that the $k_La$ values increased with temperature (Albal et al., 1984, Karandikar et al., 1986; Karandikar et al., 1987; Panja and Rao, 1992). However, in some cases the $k_La$ values decreased with an increase in temperature (Karandikar et al., 1987), while others found $k_La$ to be independent of temperature (Joshi et al., 1982, Chang & Morsi 1991).
It should be noted that there are no chemical reactions taking place in all the cases of mass transfer at elevated temperature cited above. The effects observed on $k_La$ were for physical absorption alone.

The value of the liquid phase diffusion coefficient is the major factor which influences the value of mass transfer coefficient. Agitation intensity, bubble size and bubble rising velocity have no effect on the mass transfer coefficient, but large bubbles (>2.5 mm diameter) give greater mass transfer coefficients than small bubbles (<2.5 mm diameter). The absorption mechanism in large bubbles, which are usually circulating under shear, is that of unsteady state diffusion as postulated by the penetration theory. Small “rigid sphere” bubbles move in liquids as rigid spheres. Calderbank and Moo-Young (1961) provided an expression for the mass transfer coefficient applicable for small bubbles (with size < 2 mm diameter):

$$k_L = 0.31 \text{Sc}^{-2/3} \frac{h}{C_p \rho} \text{Pr}^{2/3} = 0.31 \left( \frac{D_{Lw} \rho_A g}{\mu_L} \right)^{1/3} \text{ Eq. 2-32}$$

This correlation holds for mass transfer in mixing vessels where suspended solids and gas bubbles are undergoing dissolution. The correlation applies to those systems where particles of the dispersed phase behave as rigid bodies and where relative movement between the phases is retarded.

A direct determination of mass transfer coefficients for oxygen requires measurement of the rate of oxygen absorption into the solution in the same reacting vessel and under the same hydrodynamic conditions, but in the absence of any chemical reactions. Several devices have been tested, without reliable results, to measure the oxygen concentration in solution as a function of time. The physical mass transfer coefficient for oxygen in water has been correlated in the work of Bravo and others (Bravo et al., 1996) and is given as:

$$k_{Lw} = 1.02 \times 10^{-4} \frac{T}{\mu_w} \text{ Eq. 2-33}$$
where $\mu_w$ is the viscosity of pure water and $T$ is the absolute temperature.

However, this value is not directly relevant for the oxidative leaching systems examined in this work. To account for the physical properties of the solution, particularly viscosity, density and the diffusion coefficient of oxygen, the correlation of Calderbank and Moo-Young (1961) for mass transfer coefficients is normally used (Levy et al., 1981; Beutier et al., 1986):

$$k_L \propto \left( \frac{D}{\mu} \right)^{1/3}$$

Eq. 2-34

*The influence of electrolyte on the mass transfer coefficient*

The presence of an electrolyte greatly increases the interfacial area (Midoux and Charpentier, 1984) up to saturation at an electrolytic concentration of about 0.2 kmol/m$^3$. The saturation threshold is a function of the nature of the electrolyte only. The maximum increase in interfacial area is also a function of the nature of the electrolyte. For example, the interfacial area is 25% greater for solutions of $\text{Na}_2\text{SO}_4$ than for solutions of $\text{NaCl}$ under the same conditions. This tendency indicates that polyvalent ions are more active than monovalent ions. Generally, ions in solution inhibit coalescence and favour large surface areas.

The presence of electrolytes in water tends to aid in the existence of smaller bubbles due to surface tension and the electrostatic potential of the resultant ions at the liquid surface (Sideman et al., 1966). These effects are found in intensely agitated systems and unagitated systems alike (Yoshida et al., 1960). For instance, under the same conditions oxygen absorption in sodium sulphite per unit volume of liquid in the absence of catalyst was found to be faster than in pure water, especially under high agitation. Smaller bubbles were observed in the sodium sulphite solution compared to those produced in pure water under the same conditions. It was also found that sodium sulphate solution absorbed oxygen as rapidly as that of sodium...
sulphite. The two solutions are considered to have similar physical properties. Since sodium sulphate does not react with oxygen, it was concluded that the difference between the rates of absorption of oxygen in pure water and in the sodium sulphite solution resulted from smaller bubbles and greater interfacial area in the sodium sulphite solution rather than from chemical reaction. Similar rates were found when the oxygen absorption was determined in terms of the rate of absorption per unit interfacial area, implying that the rate of absorption per unit volume was accelerated because of the greater interfacial area induced by the presence of ions. The hydrophilic solutes act to prevent coalescence of small bubbles into bigger bubbles. This is true for all electrolyte solutions and can be explained by the electrostatic potential of the resultant ions at the liquid interface. Interdispersion of immiscible fluids is brought about by fluid dynamical forces, which have to overcome the static force of surface tension. Such surface forces resist dispersion by attempting to retain bubble or drop sphericity and prevent gross distortion leading to breakup. This static force of surface tension may be reduced if surface active agents are present due to the adsorption of charged ions at the interface, which by mutual repulsion cause an outward electrostatic force in opposition to the inward force of surface tension. Although ionic solutions sometimes have surface tensions with insignificant difference from water, they considerably increase the specific interfacial area. On the other hand, increase in the electrolyte concentration reduces the diffusion coefficient (as we shall see later) of oxygen and hence decreases $k_L$. Therefore any net increase in $k_La$ due to the presence of electrolyte can only be exclusively contributed by the increase in interfacial area.

The impact of surfactants on the mass transfer coefficient

Surface active agents cause the high mass transfer coefficients for large bubbles to be reduced to those obtained with rigid spheres (Calderbank and Moo-Young, 1961). Studies of the influence of surface tension on the interfacial area show that the interfacial area increased rapidly by a factor of 6
as the surface tension decreased to a certain value, where it then leveled off (Midoux and Charpentier, 1984). Further decreases in the interfacial tension did not produce any increase in interfacial area. It was therefore concluded that the surfactant effect is not strongly tied to the static surface tension. Also, soluble surfactants have a tendency to stabilize small bubbles and to prevent their coalescence. However, surfactants do not impede the fraction of large bubbles.

Liquid phase mass transfer near the free gas-liquid interface involves molecular diffusion, small-scale eddy diffusion and large-scale surface renewals. Addition of a surfactant such as a protein monolayer at the same stirring speed causes the mass transfer rate to decrease dramatically (Davies, 1964). Surfactants were observed to cause gas-liquid interfaces to become rigid. The rigidity suppresses the surface renewal mode of mass transfer. Hence, gas-liquid mass transfer in the presence of surfactants increasingly depends on the slow process of molecular diffusion.

The presence of surface-active agents (surfactants) could reduce the transfer coefficient to values as low as 30% of those measured in the absence of these agents (Davies, 1964). Flow patterns around the bubbles and the structure of the interface itself indicate a large influence that traces of surface active material may exert on gas-liquid mass transfer systems. Trace quantities of surfactants may be sufficient to exert a marked influence. Hence, surface active contamination or addition must always be considered as a possible hidden variable in these systems (Hyman, 1962).

Experimental results show that similar $k_La$ values can only be found if the system properties are identical. For example, Chaudhari et al. (1987) found that the values of $k_La$ determined by the oxidation of sodium sulphite, the catalytic hydrogenation of styrene, and by absorption (hydrogen-ethanol system) agreed closely with each other. In this case, while the presence of sulphite ions caused a non-coalescing medium, styrene and alcohol (ethanol) have similar non-coalescing properties. On the other hand, the acetylene-
water system for physical absorption gave lower values of $k_La$ under similar operating conditions because the properties of this system do not prevent the coalescence of bubbles.

A conclusion of practical interest is that high mass transfer coefficients for large bubbles in unhindered flow can only be realized under special circumstances. In industrial situations of high gas flow rates, surface active impurities and deep liquid pools, the mass transfer coefficients will approach the lower values obtained for rigid spheres (Calderbank and Moo-Young, 1961). Also, the hydrometallurgical systems considered in this work involve ions of sufficiently high concentration to guarantee the rigid behaviour of small bubbles. Therefore, the mass transfer coefficient correlation for small bubbles was used.

The influence of gas pressure on mass transfer coefficient

Gas-liquid reactions of hydrometallurgical importance are often conducted under pressure. Since the overall reaction rate of some reaction systems may be found to be limited by the liquid phase resistance to mass transfer, the variation of the liquid phase mass transfer coefficient with pressure is of great importance. Yoshida and Arakawa (1968) reported a decrease in the liquid-phase mass transfer coefficient $k_L$ with increasing pressure at moderate pressures. This phenomenon was observed during the absorption of oxygen in water and in a dilute aqueous potassium iodide solution. They suggested that the change might have been due to changes in the rate of surface renewal or the degree of interfacial tension caused by the gas pressure. Similar declining dependence of the transfer rate on the pressure as pressure was increased from one to two atmospheres was observed by Phillips (1973). However, hydrodynamic characteristics appeared to be the same at both pressures. Therefore, the cause for this behaviour was attributed to a simultaneous absorptive and adsorptive oxygen transferring mechanism from the gas to the liquid phase.
Contrary to the above observations, Teramoto et al. (1974) found that $k_La$ values were independent of the pressure for a number of gases absorbed into water at 25°C. They considered a pressure range from 2 to 100 atm. Although oxygen was not included in this study, they concluded it was unlikely that the absorption of oxygen could show any substantial difference in behaviour. The fact that physical properties of liquids and aqueous solutions such as density, viscosity and diffusivity vary negligibly in the pressure range studied was pointed out as the reason behind the invariance of $k_L$. The pressure effect could be important for some organic compounds such as $p$-xylene because their viscosities are more susceptible to the effect of pressure than is the viscosity of water. The pressure dependence of $k_L$ for such a case could be explained by taking into account the change in liquid phase diffusivity and viscosity with pressure. It was pointed out that the time lag encountered when membrane electrodes are used (Yoshida and Arakawa study) compared to the use of strain gages (Teramoto et al. study) could be the reason for the observed decrease of $k_L$ with pressure in the former study. Normally the effect of pressure on the mass transfer coefficient is, for all practical purposes, ignored. In this study the effect of pressure on the mass transfer coefficient will not be considered.

The effect of solids

Often hydrometallurgical processes require the presence of gas, liquid and solid phases. The solids might be inert, catalytic or reactive. It is therefore important to examine the possible impact produced by the presence of solid particles on the volumetric mass transfer coefficient.

The effect caused by the presence of solids in a liquid on the volumetric mass transfer coefficient $k_La$ depends on particle nature, particle size and solids concentration in the gas-liquid system. Generally, the effect of solids can be ignored at low solids loading. However, at higher concentrations, the presence of solids must be accounted for because it influences the rate of
mass transfer by affecting either $k_L a$, or both. The reduction of $k_L a$ in the presence of solids might be due to a diffusion blocking effect (Lee et al., 1982) or the dampening effect of the interfacial turbulence (Kada and Harrantly, 1960). The interfacial area is affected by the presence of inert solids through an increase in apparent viscosity and altered bubble coalescence rates (Mills et al., 1987).

Mehta and Sharma (1971) observed that a small quantity of solids (as low as 3% w/v 3CuO·CuCl₂·3H₂O) caused a 25% decrease in the value of $k_L a$ for cuprous chloride solutions. Other investigators also found a decrease in $k_L a$ when inert solids of either hydrophilic particles or hydrophobic particles were added to liquids. Mills et al. (1987) found that the volumetric mass transfer coefficient for oxygen in a mechanically agitated vessel containing 66 μm glass beads decreased with increasing solids loading. A reduction of 65% in the value of $k_L a$ was observed at a glass beads concentration of 40% v/v. Cheng (1994) found that the addition of both hydrophilic as well as hydrophobic inert solid particles decreased the value of $k_L a$.

An increasing trend in $k_L a$ has been reported when the particles are activated carbon. Chandrasekaran and Sharma (1977) reported a 60% increase in $k_L a$ in the presence of 0.2% w/w activated carbon. Alper et al. (1980) found that $k_L a$ in slurries of 0.1 – 3.3% w/w activated carbon were 150% higher than those determined in the presence of quartz or sand.

It is evident that solids present in hydrometallurgical gas-liquid systems are not always inert. Most of the particles found in hydrometallurgical systems such as pressure leaching are reactive. The presence of fine, sparingly soluble, solid reactant particles increases the rate of oxygen transfer into slurries (Mehra, 1996). The mass transfer coefficient is enhanced by the reaction between gas and fine particles or gas and dissolved solid species in the liquid film. For such a phenomenon to occur, the size of the reactive particles must be less than the thickness of the liquid film (Uchida et al., 1975).
From the foregoing literature information the presence of solids in liquids poses a challenge in investigating oxygen transfer. Therefore, although the ultimate goal of any study aimed at comprehending oxygen mass transfer in hydrometallurgical reactors must deal with slurries, the complexity of studying such systems suggests that systematic studies of oxygen mass transfer begin with leaching solutions.

*Oxygen diffusivity, \( D_A \)*

Knowledge of the diffusivities of gases through aqueous electrolytes is very important in hydrometallurgical reactor design, particularly in cases where the absorption of gases is accompanied by chemical reactions. The gas diffusivity is not only required for Hatta number calculations but also in determining the influence of temperature on the liquid-phase mass-transfer coefficient. The effect of temperature on \( k_L \) could be explained mainly by the variations in liquid phase viscosity and diffusion coefficient with temperature (Whitney and Vivian, 1949). Experimentally obtained data on diffusivities are not extensive, because accurate measurements are difficult and tedious (Ratcliff and Holdcroft, 1963). The few that are available were determined at ambient conditions. The need to use theoretically predicted values cannot be overemphasized. For a satisfactory prediction of the diffusivity of a gas in a mixture of electrolytes, forces between individual molecules in the liquid phase must be taken into account. An empirical correlation is available for predicting the gas diffusivity in aqueous solutions of mixed electrolytes at 25°C and 1 atm (Hikita et al., 1979; Hikita et al., 1978). For mixed electrolyte solutions the gas diffusivity is given by the expression:

\[
\frac{D_A}{D_{A-w}} = 1 - \sum_{i=1}^{n} \varepsilon_i C_i \quad \text{where} \quad \varepsilon_i = 0.03 + 0.55\omega_i \quad \text{Eq. 2-35}
\]

and where \( \varepsilon_i \) and \( \omega_i \) are empirical constants. The constant \( \omega_i \) can be evaluated from viscosity data using the relationship:
Several researchers who accounted for the effect caused by the presence of electrolytes have applied the equation to oxygen diffusivity through electrolytes (Sevilla et al., 1990; Tran and Swinkels, 1986; Bravo et al., 1996). Although the original correlation was based on experiments carried out using carbon dioxide as the diffusing gaseous solute, it is believed to hold true for oxygen which is also a sparingly soluble gas in most electrolyte solutions.

The Stokes-Einstein equation (eq. 2-37) has, in general, been found to be less satisfactory in predicting the effect of electrolytes on gas diffusivities in solution, typically predicting values which are too low (Ratcliff and Holdcroft, 1963). Despite its failure to account for the effect caused by the presence of an electrolyte in aqueous solutions, once this effect is corrected, the Stokes-Einstein equation is effective in correcting for the effect of changes in viscosity and temperature on the diffusivity of the gas (Seville et al., 1990). The liquid phase diffusion coefficient may be corrected from the base temperature to another temperature using the Stokes-Einstein relation as recommended by Wilke (1949). The Stokes-Einstein law is expressed as:

\[
\frac{D_{A-W} H_w}{T} = \text{constant}
\]

Eq. 2-37

The value of the oxygen diffusion coefficient in pure water at 25°C is published in the literature (Perry and Green, 1984). Alternatively, a correlation put forward by Bravo and his co-workers (Bravo, 1996) gives a comparable value at 25°C:

\[
\frac{D_{A-W} H_w}{T} = 7.22 \times 10^{-9}
\]

Eq. 2-38

The actual value of the diffusion coefficient in solution, at working temperature, was then found by substituting the viscosity of solution at 25°C
by that at the working temperature. The values of diffusivity obtained were utilized to compute the corresponding mass transfer coefficients.

2.2.3.2 Effect of temperature on the reaction rate constant, $k$

The kinetic rate constant $k$ is temperature dependent and is expected to increase with increasing temperature. The Arrhenius rate law normally estimates the dependence of reaction rate constant on temperature:

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} \text{Eq. 2-39}

This estimation can only be used to obtain the kinetic rate constant if the activation energy is known. The Arrhenius relation gives straight lines in a plot of $\log k$ versus $T^{-1}$. From their slopes values of $E_a$ can be deduced.

2.2.4 Oxygen solubility, $C_A^*$

Solubility of oxygen in leaching solutions is important because both diffusion and chemical reaction rates depend on the concentration of the dissolved gas. Oxygen is a sparingly soluble gas with very low solubility in water and aqueous solutions of interest to hydrometallurgy. The solubility of oxygen in water may increase, decrease or decrease and then increase with increasing temperature depending on the temperature range. For instance, at an oxygen partial pressure of 101.325 kPa in the gas phase the solubility of oxygen in pure water was reported to be about 0.002 mol/L at 0°C (Benson et al., 1979). The value drops to less than 0.001 mol/L at 100°C before it rises again above the water boiling temperature. A similar trend is followed when oxygen is absorbed in leaching solutions. Therefore, the effect of temperature on gas concentration depends on the temperature range at which the reaction takes place and the nature of the gas under consideration. However, the presence of dissolved mineral salts, acids and bases in leaching solutions significantly decrease the oxygen solubility compared to its value in
pure water. The plot of oxygen solubility versus temperature in solutions of
sulphuric acid, ferric and zinc sulphate is depicted in Figure 2-5.

Several correlations have been advanced to express the relationship
between oxygen solubility in water and operating temperature. For the
temperature range of 273 to 348 K, Battino (1981) fitted the solubility data in
terms of mole fraction to the equation:

\[
\ln x_A^* = -179.344 + 8747.55 \frac{T}{T^2 - 24.4526 \ln T}
\]

Eq. 2-40

where \( x_A^* \) is the mole fraction solubility of oxygen. This temperature range is
too narrow to cover most of the conditions employed in hydrometallurgy.

The solubility of sparingly soluble gases such as oxygen can also be
related to their partial pressures using Henry's law:

\[
\rho_A = x_A^* H
\]

Eq. 2-41

in the pressure range where the gas obeys the ideal gas law. Therefore, an
empirical expression was presented by Fernández-Prini and Crovetto (1989)
relating the Henry's law constant for oxygen in water with temperature. For
the temperature range encountered in hydrometallurgy, 273 to 573 K, the
Henrian coefficient is given by:

\[
H = 10^9 \exp(-15.9766 + 1.57951 \times 10^4 T^{-1} - 4.3331 \times 10^6 T^{-2} + 3.502 \times 10^8 T^{-3})
\]

Eq. 2-42

The equation above is said to have a relative standard deviation of
about ±5%. Another semi-empirical correlation for the Henrian coefficient of
oxygen in water was put forward by Harvey (1997) covering the temperature
range from 273 to 616 K:

\[
H = \rho_w \exp \left[ -9.40325 \frac{T_{cr}}{T} + 4.4923 \left( 1 - \frac{T}{T_{cr}} \right)^{0.355} \left( \frac{T_{cr}}{T} \right) \right] + 11.3387 \left( \frac{T_{cr}}{T} \right)^{0.41} \exp \left( 1 - \frac{T_{cr}}{T} \right)
\]

Eq. 2-43
Figure 2-5  Oxygen solubility in zinc pressure leaching solutions expressed as mole fraction for a partial pressure of 101.3 kPa (Hayduk, 1991)
In this equation \( p_w \) is the water vapour pressure and \( T_{cr} \) is the critical temperature. This equation can be employed to estimate Henrian coefficients of several gases dissolved in water or other liquids. However, it requires the knowledge of the critical temperatures of the liquid and the corresponding vapour pressures.

Tromans (1998a) provided a comprehensive equation on oxygen solubility in pure water, based on thermodynamic analysis and experimental data from various sources. This particular equation covers the temperature range from 273 to 616 K and up to 6.08 Mpa (60 atm) pressure. It is simplified by the fact that the oxygen solubility is presented as a function of the operating temperature and pressure only. The molal oxygen solubility is given by the expression:

\[
m_{A,w}^* = \rho_A \exp \left( \frac{0.046 T^2 + 203.35T \ln(T / 298) - (299.378 + 0.092 T)(T - 298) - 20591}{8.31447} \right)
\]  

Eq. 2-44

where \( \rho_A \) is in atm. This value can be converted to molar units using the equation:

\[
C_{A,w}^* = p_w m_{A,w}^*
\]  

Eq. 2-45

### 2.2.4.1 Oxygen solubility in electrolyte solutions

The concentration of oxygen at the interface will be its equilibrium concentration, which is normally estimated by its solubility in the liquid. Oxygen solubility in inorganic aqueous solutions is usually lower than that in pure water (Clever, 1981). However, a similar influence of temperature on solubility is observed in electrolyte solutions. In the pressure leaching solutions used for zinc sulphide leaching for example, it was found that the oxygen solubility is reduced to 40% of that in pure water (Hayduk, 1991). This tendency is due to the salting out effect, which refers to the phenomenon whereby the addition of a solute to a solution decreases the solubility of another, in this case oxygen. The salting out behaviour has been attributed to
the greater attraction between ions and water molecules than between non-polar or slightly polar gas molecules and water.

Inorganic solutes when dissolved in water decrease the oxygen solubility to an extent dependent on the solute characteristics in aqueous solution. For instance, in the report by Hayduk the influence of zinc in reducing the oxygen solubility was higher than that of sulphuric acid of the same concentration. The most common electrolytes in hydrometallurgy are those of acids, salts and other dissolved mineral solutes.

Sechenov (Battino, 1981) was the first to attempt expressing the salting out of oxygen by electrolytes mathematically:

\[
\log \left( \frac{C_A^*}{C_{A,w}} \right) = K_{Se} C_i
\]

where \( K_{Se} \) is the Sechenov constant and \( C_i \) is the electrolyte concentration. The Sechenov equation could be used with concentrations in molalities, molarities or mole fractions. The Sechenov constant (also known as the salting out coefficient) depends on the gas-aqueous solution system and on temperature. It is evident that experimental data are therefore needed to evaluate the constant at the desired temperature rendering the estimation of oxygen solubility in the absence of experimental data impossible.

An improved version of the preceding equation is the method proposed by Van Krevelen and Hoftijzer (Hikita et al., 1977; Charpentier, 1981) which also relates the oxygen solubility in solution to that in pure solvent at the same temperature:

\[
\log \left( \frac{C_A^*}{C_{A,w}} \right) = hI
\]

where \( I \) is the ionic strength given as:

\[
I = \frac{1}{2} \sum C_i Z_i^2
\]
In this equation $C_i$ is the concentration of ions of valence $Z_i$. The salting out parameter $h$ is expressed as the sum of contributions of the positive and negative ions present and the gaseous species:

$$h = h_g + h_+ + h_- \quad \text{Eq. 2-49}$$

For a mixed electrolyte, it is assumed that the solubility may be represented by an expression of the form:

$$\log \left( \frac{C_{A}^{*}}{C_{A,w}^{*}} \right) = h_1 I_1 + h_2 I_2 + \ldots \quad \text{Eq. 2-50}$$

In this equation $I_1$ stands for the ionic strength attributable to species 1 of the electrolyte and $h_1$ is a coefficient characteristic of the electrolyte. The ion-specific parameters $h_i$ for various ions are presented in Table 2-1.

The major drawback of these equations is that they are based on the assumption of complete ion dissociation. Hence they cannot be applied for more concentrated solutions except for strong electrolytes that dissociate completely even at higher concentration. The equations underestimate oxygen solubility in solutions of weak electrolytes such as ammonia. A formula put forward by Narita et al. (1983), seems to overcome this problem by taking into account the actual concentration of all species in the solution:

$$\log \left( \frac{C_{A,w}^{*}}{C_{A}^{*}} \right) = \sum_i K_i C_i \quad \text{Eq. 2-51}$$

where $K_i$ is a constant depending on each ion. The equation still suffers from temperature limitations.

A thorough expression for oxygen solubility was again put forward by Tromans (1998b, 2000) as an extension to the equation for oxygen solubility in water. In short, the oxygen solubility in a solution is obtained by multiplying its solubility in water by a factor representing the amount of water in the solution that is available for oxygen to dissolve in. The rest of the water is considered to be permanently interacting with the dissolved ions of
the inorganic solute. The ion-water interactions accounted for in calculating the free water fraction are both primary and secondary hydration. This factor is ion specific and depends on the molal concentration of each ion in the solution and its corresponding ionic strength. The molal solubility of oxygen is then the product of the fraction of water available and oxygen solubility in water:

\[ m^*_A = \varphi m^*_{A,w} \]  
\[ \text{Eq. 2-52} \]

where the factor \( \varphi \) is given by the function:

\[ \varphi = \left( \frac{1}{1 + \kappa(C_i)^y} \right)^\eta \]  
\[ \text{Eq. 2-53} \]

The coefficient \( \kappa \) and the exponents \( y \) and \( \eta \) are solute specific and are positive. The \( \varphi \) factor was obtained by fitting experimental oxygen solubility data into the solubility equation. Then, the experimental factor values were fitted to the available water factor function to get \( \kappa, y \) and \( \eta \) for each electrolyte present in the solution.

For a multi-electrolyte solution, with electrolytes \( I_1, I_2, \ldots, I_n \) and individual available water factors \( \varphi_1, \varphi_2, \ldots, \varphi_n \), arranged in increasing order, the overall effective available water factor \( \varphi_{\text{eff}} \) will be dominated by the smallest \( \varphi \) factor of one electrolyte, say \( \varphi_1 \). The larger available water factors of the other electrolytes adjust this factor by a multiplying function represented by:

\[ \varphi_{\text{eff}} = \varphi_1 \left( \prod_{i=2}^{n} \varphi_i \right)^q \]  
\[ \text{Eq. 2-54} \]

where \( \prod_{i=2}^{n} \varphi_i \) is the product of \( \varphi_2 \times \varphi_3 \times \cdots \times \varphi_n \), and \( q \) is an empirical exponent.

The ultimate equation for the molal oxygen solubility in a multi-electrolyte aqueous solution is given in the form:
The value of \( q \) is estimated from the calculation for the available water factor. It is assumed that an aqueous solution of one electrolyte alone has a total concentration of 1.5 m. Further assumption is made that the solution could be treated as containing three electrolytes each of concentration 0.5 m with three available water factors \( \varphi_1, \varphi_2 \) and \( \varphi_3 \) of the same value \( \varphi_{0.5m} \). From these assumptions and the effective available water factor, \( \varphi_{eff} \), the value of \( q \) can be evaluated as:

\[
q = \frac{\log \varphi_{eff} - \log \varphi_{0.5m}}{2 \log \varphi_{0.5m}}
\]

Eq. 2-56

All these equations require experimental data to evaluate the available water factor, \( \varphi \). Therefore, they can only be used in the presence of experimental values. Also, the model is based on the assumption of completely dissociated electrolytes. In highly concentrated solutions, where electrolytes may be only partially dissociated, oxygen solubility might be underestimated. Values for the exponents \( y \) and \( \eta \) and the coefficient \( k \) as evaluated by Tromans (2000) are presented in Table 2-II. This method gives the oxygen solubility in terms of mol/kg of water. Such values were converted to mol/L units through the following expression:

\[
C_A^* = m_A^* \rho_s (1 - f)
\]

Eq. 2-57

where \( \rho_s \) is the solution density and \( f \) is the mass fraction of the solution consisting of dissolved solutes.

It is worth mentioning that when oxygen solubility was estimated under zinc pressure leaching conditions using the Tromans (1998b) procedure, the results obtained were lower than those determined experimentally. Tromans suggested that there was still a possibility of corrosion that affected the
experimental results. However, it was observed during the oxygen solubility experiments that solutions containing ferric iron produced some precipitates, especially at temperatures in excess of 100°C (Kimweri, 1990) meaning that less salt was dissolved at the operating temperature. The precipitates produced weighed far more than the initial ferric salt added showing some possibility of zinc sulphate inclusion. It is possible that precipitates reduce oxygen solubility to a lesser extent compared to dissolved electrolytes. Chemical analysis of samples taken for similar precipitates during the course of this work indicated that they contained zinc, ferric and minute amounts of titanium. Furthermore, given the way in which the oxygen solubility was determined, a uniform corrosion for all experiments would have to be guaranteed for any interference by corrosion to go unnoticed. All experimental data had to pass an oxygen volume versus solution volume straight-line plot criterion. Again, in cases where air was used as the source of oxygen, the desorbed gas was passed through a gas chromatograph to analyze its composition. There was no additional gas detected. Moreover, the zinc pressure leaching solutions used in this work contained a substantial amount of iron, both ferric and ferrous iron. However, the Tromans procedure does not provide a means to estimate the effect of iron on oxygen solubility.
### Table 2-I  Ion-specific parameters, $h_i$ (Hermann *et al.*, 1993)

<table>
<thead>
<tr>
<th>Cation</th>
<th>$h_{i_i}$ (L/mol)</th>
<th>Anion</th>
<th>$h_{i_i}$ (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>0.0000</td>
<td>OH$^-$</td>
<td>0.0918</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.0687</td>
<td>F$^-$</td>
<td>0.1058</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.1079</td>
<td>Cl$^-$</td>
<td>0.0381</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.0929</td>
<td>Br$^-$</td>
<td>0.0266</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>0.0749</td>
<td>I$^-$</td>
<td>0.0233</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>0.0582</td>
<td>NO$_2^-$</td>
<td>0.0726</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.0555</td>
<td>NO$_3^-$</td>
<td>0.0136</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.1576</td>
<td>ClO$_3^-$</td>
<td>0.1390</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.1543</td>
<td>BrO$_3^-$</td>
<td>0.0549</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>0.1710</td>
<td>IO$_3^-$</td>
<td>0.1158</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.1694</td>
<td>IO$_4^-$</td>
<td>0.0956</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>0.1582</td>
<td>HCO$_3^-$</td>
<td>0.1469</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.1556</td>
<td>HSO$_3^-$</td>
<td>0.1019</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.1490</td>
<td>H$_2$PO$_4^-$</td>
<td>0.0601</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.1474</td>
<td>OCH$_2$COO$^-$</td>
<td>0.1009</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.1588</td>
<td>CN$^-$</td>
<td>-0.0089</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>0.2028</td>
<td>SCN$^-$</td>
<td>0.0722</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.2192</td>
<td>HCrO$_4^-$</td>
<td>0.0670</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.0957</td>
<td>HPO$_4^{2-}$</td>
<td>0.0408</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.0578</td>
<td>NO$_3^-$</td>
<td>0.1558</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S$_2$O$_3^{2-}$</td>
<td>0.1268</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>0.1357</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_4^{2-}$</td>
<td>0.1164</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO$_4^{3-}$</td>
<td>0.2243</td>
</tr>
</tbody>
</table>
Table 2-II Values of coefficient ($\kappa$) and exponents ($y$ and $\eta$) for equation to calculate the available water factor $\phi$ at 298 K and 101.325 kPa (after Tromans, 2000)

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\kappa$</th>
<th>$y$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.305514</td>
<td>1.092174</td>
<td>0.232093</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>2.01628</td>
<td>1.253475</td>
<td>0.168954</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.102078</td>
<td>1.00044</td>
<td>4.308933</td>
</tr>
<tr>
<td>KOH</td>
<td>0.102078</td>
<td>1.00044</td>
<td>4.308933</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.034541</td>
<td>0.925947</td>
<td>7.095218</td>
</tr>
<tr>
<td>KBr</td>
<td>0.034541</td>
<td>0.925947</td>
<td>7.095218</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.075502</td>
<td>1.009502</td>
<td>4.223927</td>
</tr>
<tr>
<td>KCl</td>
<td>0.407374</td>
<td>1.116089</td>
<td>0.842095</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.629498</td>
<td>0.911841</td>
<td>1.440175</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>0.55</td>
<td>0.911841</td>
<td>1.440175</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.119674</td>
<td>1.107738</td>
<td>5.455537</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>0.232671</td>
<td>1.010428</td>
<td>2.655655</td>
</tr>
<tr>
<td>CoSO$_4$</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>2.23207</td>
<td>1.115617</td>
<td>0.222794</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.179714</td>
<td>0.984502</td>
<td>2.71142</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.179714</td>
<td>0.984502</td>
<td>2.71142</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>0.179714</td>
<td>0.984502</td>
<td>2.71142</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>0.020554</td>
<td>0.946932</td>
<td>21.04001</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>0.38142</td>
<td>0.804022</td>
<td>1.683714</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>0.641163</td>
<td>0.954719</td>
<td>3.033594</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.57</td>
<td>1.2</td>
<td>0.278</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>0.69</td>
<td>1.11</td>
<td>0.749</td>
</tr>
<tr>
<td>(NH$_3$)$_aq$</td>
<td>0.0105</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
</tbody>
</table>
Since the experimental conditions for oxygen mass transfer covered similar conditions as those when determination of oxygen solubility was conducted, the correlation proposed by Hayduk (1991) was used to compute the oxygen solubility. In the overall correlation for temperatures higher than or equal to 95°C, the oxygen solubility expressed as g/L is given by:

\[
S = 0.0244 + 10^{-5}[0.144(T - 368)^2 - 2.6C_{\text{Ac}} - 13.2C_{\text{Zn}} - 15.0C_{\text{Fe}}]
\]  
\text{Eq. 2-58}

where \(S\) is the oxygen solubility in g/L, \(T\) is the absolute temperature in K, \(C_{\text{Ac}}\) is acid concentration, \(C_{\text{Zn}}\) is the zinc concentration and \(C_{\text{Fe}}\) is the iron concentration, all in g/L. The solubility of oxygen expressed in mol/L is then:

\[
C^*_A = \frac{P_a}{P_a M_{\text{O}_2}} \frac{S}{S_{\text{sol}}}
\]  
\text{Eq. 2-59}

where \(P_a\) is the atmospheric pressure and \(M_{\text{O}_2}\) is the molecular weight of oxygen (32.00 kg/kmol).

### 2.3 STUDIES ON CHEMICALLY ENHANCED O\(_2\) MASS TRANSFER

Previous work by Levy, Baratin and Renon (Levy \textit{et al.}, 1981) on the oxidation of Cu(I) with oxygen gas in concentrated sodium chloride solution at 20°C in an agitated vessel resulted in Hatta numbers of 2.87 and 2.55 for a flat interface with surface aeration and sparged conditions, respectively. In this case, absorption of CO\(_2\) into distilled water was employed to find the mass transfer parameters for the O\(_2\)-Cu(I) system. The Hatta numbers increased dramatically at 30°C to 23.4 and 13.9 for the same conditions when the O\(_2\)-Na\(_2\)SO\(_3\) system was adopted. Since two different gas-liquid systems were used and given the fact that absorption of oxygen in sodium sulphite is strongly affected by impurities (Charpentier, 1981), it is not possible to access the impact of raising temperature on the Hatta numbers obtained in this study.
The same reaction was used by Benadda and coworkers (Benadda et al., 1994) to evaluate the Hatta number at 20°C as a function of solution composition. Hatta numbers ranging between 0.58 to 2.25 were obtained confirming the previous study by Levy and coworkers (1981) that the oxidation of Cu(I) by oxygen in NaCl solutions is in the intermediate reaction regime.

Hatta numbers were also evaluated for the oxidation of ferrous ions with oxygen in concentrated NaCl solutions at three different low temperatures (Bouboukos et al., 1987). The values obtained were $1.03 \times 10^{-3}$ at 18°C, $2.68 \times 10^{-3}$ at 31°C and $6.44 \times 10^{-3}$ at 45°C. The Hatta numbers obtained in this study conducted in an agitated reactor put this reaction in the very slow reaction regime that is chemical reaction controlled.

Additional information concerning the effect of temperature on the Hatta number is obtained by calculating these numbers from the study of Bravo and coworkers (Bravo et al., 1996) undertaken with a flat oxygen-solution interface with surface aeration. In that study, data indicating the effect of temperature and concentration of MnSO$_4$ on the simultaneous absorption and reaction of SO$_2$ and O$_2$ were provided. From their data the calculated Hatta numbers range from 1.2 at the lowest temperature of 10°C and minimum MnSO$_4$ concentration to 4.0 at the highest temperature of 40°C and maximum MnSO$_4$ concentration. Values of the Hatta numbers obtained at different temperatures and catalyst concentrations are presented in Table 2-III.

It was possible to estimate Hatta numbers at high temperatures from the study of autocatalytic oxidation of cyclohexane conducted by Suresh and coworkers (Suresh et al, 1988a, 1988b, and 1988c). The computation of the Hatta numbers was based on several assumptions. First, the average intermediate product concentrations were assumed to be 0.55, 0.78 and 1.0 kmol/m$^3$ (the actual range was 0.55 to 1 kmol/m$^3$). Second, a 0.7 bar partial pressure of oxygen was used. Third, the diffusion coefficient of nitrogen in
cyclohexane was assumed to be the same as that of oxygen (diffusivity of oxygen and nitrogen are very similar (Lynch and Potter, 1978)). Fourth, the physical properties of cyclohexane were taken as those of the mixed cyclohexane and reaction products (Yaws and Turbough, 1975). The Hatta numbers obtained are presented in Table 2-IV.

Table 2-III  Hatta numbers for simultaneous absorption and reaction of SO₂ and O₂

<table>
<thead>
<tr>
<th>[MnSO₄], (mol/L)</th>
<th>0.0057</th>
<th>0.0079</th>
<th>0.0096</th>
<th>0.0116</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>1.2</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>20°C</td>
<td>1.8</td>
<td>2.1</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>30°C</td>
<td>2.6</td>
<td>2.9</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>40°C</td>
<td>3.4</td>
<td>3.7</td>
<td>3.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 2-IV  Hatta numbers for the autocatalytic oxidation of cyclohexane

<table>
<thead>
<tr>
<th>[Intermediate product], (mol/L)</th>
<th>0.55</th>
<th>0.78</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>413 K</td>
<td>0.03</td>
<td>0.25</td>
<td>0.44</td>
</tr>
<tr>
<td>423 K</td>
<td>0.04</td>
<td>0.35</td>
<td>0.60</td>
</tr>
<tr>
<td>433 K</td>
<td>0.05</td>
<td>0.44</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Although no data were found that could be related directly to the oxidative leaching solutions used in the present study, the Hatta numbers from the studies cited above provide a few trends of interest to the present study. At a given temperature the Hatta number increases with an increase in concentration of reactants or catalyst. A more significant increase in Hatta number is observed with increase in temperature at constant reactants or catalyst concentration. However, higher temperatures do not guarantee that the reaction takes place under the fast reaction regime. For example the
autocatalytic oxidation of cyclohexane which is operated at 140 to 160°C gave Hatta numbers that categorize the reaction as slow to intermediate. Fast reactions can also be realized at relatively low temperature, as in the case of simultaneous absorption and reaction of \( \text{SO}_2 \) and \( \text{O}_2 \) where Hatta numbers up to 4 were obtained at a temperature of 40°C.

Hydrometallurgical autoclaves are often operated at temperatures above the boiling point. The objective of this research is, among others, to study systematically the influence of high temperature on Hatta number for the oxidation of ferrous and cuprous ions by oxygen.

### 2.4 DIRECT OXIDATIVE PRESSURE LEACHING OF ZINC SULPHIDE

Before the direct extraction of zinc by pressure leaching was put into practice, almost all zinc metal was produced by the well-established roast-leach method. In this conventional method for zinc recovery, concentrates are oxidized in a roaster, transforming the sulphur content in the feed to \( \text{SO}_2 \):

\[
2 \text{ZnS} + 3 \text{O}_2 \rightarrow 2 \text{ZnO} + 2 \text{SO}_2
\]

Eq. 2-60

Other metallic concentrate components such as lead sulphide react with oxygen to form metal oxides such as \( \text{PbO} \). At the same time the different forms of iron sulphide pass through several reactions, leading to the formation of zinc ferrite. For example,

\[
4 \text{FeS}_2 + 11 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2
\]

Eq. 2-61

\[
\text{Fe}_2\text{O}_3 + \text{ZnO} \rightarrow \text{ZnFe}_2\text{O}_4
\]

Eq. 2-62

In all cases, sulphur dioxide is the product of the reactions. The zinc oxide is then dissolved to zinc sulphate in an acid leach step:

\[
\text{ZnO} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O}
\]

Eq. 2-63

After the process stream has been thickened, neutralized and purified, zinc sulphate solution is sent for electrowinning to recover the zinc metal.
The roast-leach method has many problems. The zinc ferrite (ZnFe$_2$O$_4$) formed in the roaster resists further reaction in the acid leach. Hence, additional treatment is required for the recovery of zinc (Spink and Stein, 1986). The residue must undergo hot acid leaching and super hot acid leaching to recover the zinc content. In doing so the iron contained in the ferrite is also co-dissolved increasing the iron load to be subsequently separated from the zinc solution prior to electrowinning. Both the intensified leaching of ferrite and the iron handling techniques are costly. The hot gases leaving the roasters contain SO$_2$ that has to be sent to an acid facility for the production of sulphuric acid. This requirement means that the production of zinc is dictated by the production of the acid plant. Emission of particulates as well as hot gases necessitates the undertaking of gas cleaning operations in order to improve the working environment as well as to meet restrictions on industrial emission limits.

The direct pressure oxidation process for zinc sulphide concentrates is a result of initial investigations carried out by Forward (Forward and Veltman, 1959). They did so against the conclusions reached by Björling (Björling, 1954), who in an earlier work concerning direct leaching of zinc sulphide found that the reaction rate for oxygen pressure leaching of pure sphalerite was impractically slow. A reasonably fast reaction rate was only achieved when nitric acid was added as a promoter. However, the presence of nitric acid in the final zinc sulphate solution presented some difficulties in subsequent electrowinning of the zinc metal. Björling went on to conclude that these difficulties, coupled with the problem of separating the produced sulphur from the leach residue, rendered the process of acid oxidation of zinc sulphide to be unfavourable. Despite these findings, the results of Forward indicated that zinc sulphide could readily be oxidized to zinc ion and elemental sulphur without the presence of nitric acid. The necessary conditions for carrying out the reaction were established below the melting point of sulphur. Extractions of zinc of from 95% to 99% were achieved in a batch reactor for a retention time of between 4 to 6 hours. Leaching was conducted at
temperatures below the melting point of sulphur because above this temperature the melted sulphur would coat the unreacted zinc sulphide, and hence stifle any further reaction. The difference between Björling’s work and that of Forward is that the former investigator used pure zinc blende, whereas the latter used zinc sulphide concentrate with sufficient acid soluble iron. Björling’s observation of a slow decomposition of zinc sulphide was attributed to the lack of ferric iron in the solution. At the time of their investigations the role of iron (Fe(II) and Fe(III)) was not known, and Forward’s success in pressure leaching was achieved without any deliberate addition of the iron. It is now common knowledge that the direct pressure leaching of zinc sulphide requires the presence of ferric iron in solution to enable rapid leaching. Consequently, the role of the ferrous-ferric redox couple is of great importance since it acts as an electron carrier. It is apparent that another catalyst, copper, might have also played a role in the successful extraction of zinc. Copper sulphate is almost universally used as an activator in the flotation of sphalerite and may be adsorbed on the mineral surface in amounts sufficient to catalyze the leaching of zinc sulphide (Scott and Dyson, 1968).

On the other hand, studies have indicated that zinc sulphide can be leached by ferric iron even in the absence of molecular oxygen (Scott and Dyson, 1968; Verbaan and Crundwell, 1986; Dreisinger et al., 1990). Indeed, the rates of oxidation of zinc sulphide using ferric iron under typical zinc pressure leaching conditions were comparable to what has been accomplished in an industrial scale zinc pressure leaching plant (Dreisinger et al., 1990). Residual sphalerite found in zinc calcine after roasting has been found to be leached by ferric sulphate (Scott et al., 1986). The leaching of ferric oxide in the calcine forms the ferric sulphate. The resulting ferrous iron has to be oxidized in order to form ferric sulphate that is further hydrolyzed to form settleable precipitates. Furthermore, initially low rates of leaching have been reported for tests run with natural sphalerite, but which do not contain ferric in the initial solution in a batch reactor (Jan et al., 1976).
Sufficient leachable iron is normally present in sphalerite to enable adequately rapid leaching to be accomplished at sufficiently high temperatures. Iron comes from the dissolution of marmatite (Zn,Fe)S, or as impurities in the form of pyrrhotite (Fe₇S₈) and pyrite (FeS₂). However, most of the pyrite can remain unattacked in the leach. Despite successful pilot plant tests, this low temperature process was never put to commercial application. One of the reasons was the capital cost for the large autoclave that was considered to be too high due to the long retention time required for zinc extraction under the low temperature conditions.

Leaching above the melting point of sulphur was first made feasible by feeding excess zinc concentrate to the reactor, followed by recycling of unleached concentrate after separating it and the elemental sulphur. With this arrangement, the reaction rate was increased substantially and retention time was reduced to about two hours. However, the necessity to treat residue in order to recycle the unleached zinc sulphide limited the overall process flexibility.

Two major discoveries permitted the economical use of the pressure leaching process for zinc sulphide. First, research indicated that certain water soluble, surface-active agents, such as Goulac and Quebracho could prevent sulphur from encapsulating the unreacted zinc sulphide concentrate. Small amounts of calcium lignosulphonate (lignosol) and/or quebracho are added to coalesce sulphur into droplets, thereby preventing the occlusion of the unleached sulphide particles. Operating without additives results in low zinc extractions and the production of coarse particles that tend to agglomerate and may plug lines and vessels. Surfactants have a large number of anionic groups and are thought to coalesce the sulphur by being preferentially adsorbed onto the surface of the sulphide particles, which are positively charged at low pH, thereby displacing sulphur (Arauco and Doyle, 1986). The presence of these surfactants might be expected to adversely affect mass transfer across the mineral-solution interface. However, conditions used
commercially make this effect less pronounced than the adverse effect of liquid sulphur on the mineral surfaces. Even when surfactants are used, at temperatures above 155°C sulphur polymerization causes a marked increase in the viscosity of the liquid sulphur which prevents sulphur coalescence even in the presence of surfactants (Arauco and Doyle, 1986). Other alternative soluble surfactants have been investigated (Owusu, 1993). Orthophenylene diamine (OPD) was found to be more durable and effective requiring smaller dosage compared to lignosol and quebracho. However, the cost of OPD is much higher than the former surfactants. In laboratory tests, coal has also been successfully shown to be a more convenient, effective and less expensive additive and therefore, a possible replacement for the surfactants currently in use (Barta, 1998).

Second, techniques were developed to separate elemental sulphur formed during leaching at high temperature (about 150°C) as a continuous molten phase. The two developments enabled the use of higher leach temperatures, which enhanced the reaction rates and thus reduced the capital and operating costs.

The pressure leaching system is a single unit operation replacing the conventional zinc process and eliminating the roasting of concentrate, oxide leaching in spent electrolyte and the production of sulphuric acid.

The reaction mechanisms for the pressure leaching of zinc sulphide concentrates using molecular oxygen in acidic sulphate have been studied extensively (Chalkley and Weir, 1983; Dreisinger and Peters, 1989, Dreisinger et al., 1990). Zinc pressure leaching is expressed by the overall reaction:

\[ 2 \text{ZnS} + 2 \text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow 2 \text{ZnSO}_4 + 2 \text{H}_2\text{O} + 2 \text{S}^0 \]

Eq. 2-64

However, studies carried out on the process indicated that molecular oxygen does not react significantly with zinc sulphide concentrates directly (Peters, 1987). Normally, oxygen first oxidizes ferrous iron producing a "surrogate" oxidant, ferric iron, which then does the oxidative work at the
mineral surface. Therefore, the overall reaction has been postulated as the sum of two reactions:

\[
\text{ZnS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{ZnSO}_4 + 2 \text{FeSO}_4 + S^0 \quad \text{Eq. 2-65}
\]

\[
4 \text{FeSO}_4 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O} \quad \text{Eq. 2-66}
\]

From these reactions it can be deduced that the actual gas-liquid reaction in the pressure leaching of zinc sulphide concentrates is the oxidation of ferrous iron to ferric iron by molecular oxygen as presented in Equation 2-66. This is the reaction, which can affect oxygen mass transfer in zinc pressure leaching. The oxidation of ferrous iron, in acidic sulphate solutions with molecular oxygen is employed in many hydrometallurgical processes such as purification of leach solutions or the regeneration of ferric iron leachants (Iwai et al., 1982). At ferrous concentrations typically found in zinc pressure leaching conditions, the reaction rate of ferrous oxidation has been found to be second order with respect to ferrous concentration and first order with respect to oxygen concentration. This dependence has been confirmed for all tests conducted in vigorously agitated reactors (Verbaan and Crundwell, 1986; Iwai et al., 1982; Huffman and Davidson, 1956; Dreisinger and Peters, 1989). However, it appears that there are no reports on ferrous oxidation in a flat interface reactor where the interfacial area is kept constant and limited.

In a standard zinc pressure leach, iron (ferrous) is mainly obtained from the zinc sulphide concentrate in the form of marmatite (Zn,Fe)S and pyrrhotite (Fe$_7$S$_8$). These two sources may release iron into the solution according to the following reactions:

\[
4 \text{Fe}_7\text{S}_8 + 45 \text{O}_2 + 52 \text{H}^+ \rightarrow 28 \text{Fe}^{3+} + 16 S^0 + 26 \text{H}_2\text{O} + 16 \text{SO}_4^{2-} \quad \text{Eq. 2-67}
\]

\[
4 (\text{Zn,Fe})\text{S} + 5 \text{O}_2 + 20 \text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 4 \text{Zn}^{2+} + 4 S^0 + 10 \text{H}_2\text{O} \quad \text{Eq. 2-68}
\]

Most of the pyrite (FeS$_2$) remains unattacked in the leach. A typical zinc sulphide concentrate consists of about 10% iron and less than 1% copper
(Chalkley and Weir, 1983). Approximately 5% of the non-pyritic sulphide sulphur in the concentrate may be oxidized to sulphate during pressure leaching.

From the work conducted to investigate the kinetics of the Sherritt Gordon zinc pressure leaching process (Dreisinger et al., 1990) it was concluded that the rate of oxidation of ferrous iron is favoured by an increase in the zinc sulphate concentration and an increase in temperature up to 155°C. Also the presence of copper sulphate in the leach solution increased the ferrous oxidation rate. However, it was found that increases in temperature above 155°C and increases in sulphuric acid concentration decreased the ferrous oxidation rate.

The maximum amount of oxygen in solution corresponds to the equilibrium or saturation solubility under the operating conditions. This amount has been measured for various sulphuric acid, zinc and iron sulphate salt solutions (Kimweri, 1990; Hayduk, 1991) under conditions similar to those prevailing in zinc pressure leaching. For a Cominco standard zinc pressure leaching solution at 155°C and an oxygen partial pressure of 760 kPa the solubility of oxygen was found to be 0.002367 mol/L. Furthermore, Dreisinger et al. (1990) have indicated that under zinc pressure leaching conditions the solution is depleted of oxygen, which means \( C_A^b \approx 0 \), which suggests that the oxygen mass transfer is enhanced. Therefore, the absorption equation can be reduced to, \( R = E_k L a C_A^* \). In the same work, it was reported that in the first compartment of Cominco's zinc pressure leaching autoclave, oxygen absorption rates are approximately \( 5 \times 10^{-4} \) mol/L-s. This gives a value of 0.2112 m/s for the enhanced volumetric mass transfer coefficient, \( E_k a \).

The physical mass transfer coefficient of oxygen in water as correlated by Bravo et al. (1996) is estimated to be \( 3.061 \times 10^{-4} \) m/s at a temperature of 428 K. The two values give a product of the enhancement factor and interfacial area, \( E_a \), of about 690 m\(^{-1}\) for the pressure leaching process. The
actual enhancement is expected to be larger than the one that could have been estimated here because the oxygen mass transfer coefficient for the leach solution will be lower than the corresponding value in water. The mass transfer coefficient is a function of the fluid properties at the interface and solution concentration. This fact will lead to a larger enhancement factor, which for a fast reaction corresponds to the Hatta number.

It is not clear whether the large value of $(E-a)$ is due to the large interfacial area or large enhancement factor. None of these values are known for the pressure leaching solutions at typical operating conditions. In this work the enhancement factors and the corresponding Hatta numbers are evaluated.

2.5 OXIDATION OF COPPER (I) IN SULPHATE MEDIA

The reaction of interest here is that between Cu(I) ions and oxygen as represented by Equation 2-69 below. The thinking behind this approach is that cupric ions oxidize sulphidic minerals of copper and possibly those of iron at high temperature (180 – 220°C) and are themselves reduced to cuprous ions. In short, a reaction mechanism similar to what had been observed in the pressure leaching of zinc sulphide (Veltman and Bolton, 1980) is assumed. Such a mechanism has been put forward for the oxidation of copper sulphide minerals and concentrates in chloride media. In the temperature range considered here, the solubility of ferric ion, which is known to oxidize such sulphide minerals in sulphate media, is very low and hence its activity. Therefore, if a reaction mechanism similar to that of zinc sulphide oxidation takes place, the most probable surrogate oxidant would be the cupric ion. The temperature range stated above refers to the conditions used in the total oxidation of chalcopyrite or pyrite as applied in the extraction of copper and the pretreatment of refractory gold minerals or concentrates in sulphate pressure leaching, respectively. Copper has been found to catalyze the pressure leaching of zinc sulphide even in the absence of iron (Scott and
Dyson, 1968). This capability is possibly extended to other sulphide minerals including those of iron and copper.

Ferreira (1975) has drawn Eh-pH diagrams for oxides and sulphides of copper at 25, 100 and 150°C. It is a well-established fact that at 25°C the cuprous ion is not stable simply because its activity is negligible. At higher temperatures, however, the results obtained are different. The cuprous ion, which is unstable at 25°C, has a significant zone of stability at 100 and 150°C. The Eh-pH diagram for copper species at 150°C is presented in Figure 2-6. From the figure it is shown that Cu metal is first oxidized to Cu(I). Since the Cu metal zone lies below the Cu(I) stability zone, it is very unlikely that the oxidation of Cu metal to Cu(II) can occur directly. In brief, Cu(I) can be neglected at 25°C but at 100 and 150° there is already a significant region within which Cu(I) is stable. The stability zone for Cu(I) increases with increase in temperature. Therefore it is expected that at 200°C Cu(I) is even more stable.

Cuprous ions have been observed when sulphide copper minerals are leached in chloride media in the absence of oxygen (Ruiz et al, 1998). If leaching is carried out in the presence of oxygen, the dissolved cuprous ions oxidize to cupric according to the reaction:

$$2 \text{Cu}_2\text{SO}_4 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{CuSO}_4 + 2 \text{H}_2\text{O}$$

Eq. 2-69

It appears that no kinetic equations have been proposed for the oxidation of cuprous to cupric in the sulphate system. The main reason is the near nonexistence of cuprous in the sulphate system at ambient conditions and hence the inability to analyze for cuprous.
Figure 2-6  Equilibrium diagram for copper oxides and sulphides in water at 423 K and 1 atm pressure. Activities of copper containing ions $10^{-3}$ and $10^{-6}$ M; sulphur containing ions $10^{-1}$ M (Ferreira, 1975)
It has been reported that during the leaching of copper sulphide with cupric chloride under an inert atmosphere, the leaching reactions are limited by chemical equilibrium (McDonald et al., 1984). The leaching of sulphides could not go to completion, as the reaction could not proceed when equilibrium between cuprous and cupric species in solution was attained. This phenomenon was observed even in situations where a significant amount of cupric ion remained in solution. It was concluded that the equilibrium reaction controlled the extent of cupric reduction in the cupric chloride leaching of chalcocite, digenite and chalcopyrite.

If the presence of oxygen results in the oxidation of cuprous ions according to reaction 2-69, then the presence of oxygen in the leaching system causes the regeneration of the cupric ions, thus allowing the dissolution to continue. Also, the presence of oxygen in the system could cause the direct oxidation of digenite and covellite (Ruiz et al., 1998) through reactions represented by the equations:

\[
\begin{align*}
&\text{Cu}_{1.8}\text{S} + 3.6\text{H}^+ + 0.9\text{O}_2 \rightarrow 1.8\text{Cu}^{2+} + 1.8\text{H}_2\text{O} + \text{S}^0 \quad \text{Eq. 2-70} \\
&\text{CuS} + 2\text{H}^+ + 0.5\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O} + \text{S}^0 \quad \text{Eq. 2-71}
\end{align*}
\]

During the actual leaching process, each of the reaction paths or all of them could proceed depending on the prevailing conditions.

Although Cheng and Lawson (1984), who studied the leaching of synthetic chalcocite in acidic oxygenated sodium chloride solutions, concluded that the reaction proceeds through the direct attack of acid and oxygen on chalcocite, most researchers have found that cupric chloride has a direct role in the leaching of copper sulphides. The study of Cheng and Lawson quoted above did not thoroughly investigate the role of the cupric chloride formed during the chalcocite leaching. Their experiments were conducted with a constant initial weight of 2 grams chalcocite in an oxygenated \text{H}_2\text{SO}_4-\text{NaCl} solution. The dissolution of chalcocite is a two step process, with a very fast first stage resulting in covellite (\text{CuS}) as the solid product formed at the end.
of the first step. Hence, experimental runs carried out under the same conditions would begin the second stage leaching at almost the same cupric concentration. In this way the effect of cupric chloride could not be elucidated.

On the other hand Hirato et al. (1987) found that during ferric chloride leaching of chalcopyrite in the absence of oxygen, the generated cupric chloride takes the place of ferric leachant during the later stages of leaching. Studies have indicated that cupric chloride is a more reactive reagent than ferric chloride (Peters and Jones, 1976; Hirato et al., 1986). Cupric chloride is also known to be an effective leachant of copper sulphides where cupric chloride itself is reduced to the cuprous state (Hirato et al., 1986). The homogeneous oxidation of Cu(I) by oxygen is very fast in chloride media. The absorption rate of oxygen gas into the aqueous phase controls the oxidation rate of Cu(I).

Another study that investigated the role of cupric ions in the leaching of copper sulphides also in the absence of oxygen was that of O'Malley and Lindel (1987). In their investigation of ferric chloride leaching of chalcopyrite, the concentration of the solution components was determined as a function of time. They observed that in the first stage of the reaction, when the concentration of ferric ions in the solution was high, there was almost no univalent copper in the liquor. However, after the ferric concentration dropped to a certain lower level, there was a dramatic and fast increase in the concentration of cuprous ions. Also at this stage the rate of leaching of chalcopyrite increased markedly, indicating that cupric ions became active in the leaching and the chalcopyrite dissolution was very rapid.

Results obtained by Ruiz et al. (1998) in the leaching of digenite with CuCl₂ in an HCl and NaCl solution showed that copper extraction increased appreciably with increasing initial cupric ion concentration in the absence of oxygen. However, the extraction reached a maximum value after a few minutes. Even with a cupric concentration of 4 times the required
stoichiometric amount to dissolve all the copper concentrate, the extraction of copper did not go to completion. This is further evidence that the copper extraction was limited by the chemical equilibrium prevailing in the leaching system. When oxygen was added to the system they found that dissolution of the copper from the copper sulphides was no longer limited by the chemical equilibrium since the cuprous ions were oxidized to cupric ions by oxygen. Furthermore, the leaching rate depended on the initial cupric ion concentration implying that the leaching of the copper sulphides proceeded by the reaction of the cupric ions with the sulphides. From this study they also observed that initially a large amount of cuprous ions accumulated in the solution, but as the leaching proceeded the concentration of cuprous ions decreased rapidly to negligible levels. In contrast, the concentration of cupric ions increased steadily throughout the leaching period. This behaviour is sufficient proof that once a small amount of cupric ion was formed by the reaction between acid, oxygen and the minerals, the leaching then proceeded mainly through the reaction of cupric ions with the copper sulphides. This reaction was accompanied by the oxidation of the cuprous ions, produced by the leaching reaction, by dissolved oxygen as represented by Equation 2-69. The kinetics of this homogeneous oxidation of Cu(I) by oxygen gas is reported to be fast in chloride media. The absorption rate of oxygen gas into the aqueous phase controls the oxidation rate of Cu(I) in the chloride system (Jhaveri and Sharma, 1967; Tran and Swinkels, 1986; Beutier et al., 1986) Therefore, one of the main requirements for this reaction was recommended to be the provision and maintenance of a high interfacial area between the solution and oxygen by dispersing the oxygen as small bubbles.

The total oxidation of copper concentrates has been successfully conducted in the sulphate system at laboratory scale over a temperature range of 170 to 220°C (King et al., 1993). Copper dissolution from different types of copper sulphide concentrates was found to increase with increasing temperature and residence time. There was no attempt to investigate the influence of oxygen partial pressure, agitation speed and initial cupric ion
concentration. Therefore, little can be discerned concerning oxygen mass transfer from that study.

Stanczyk and Rampacek (1963) investigated the leaching of bornite, chalcopyrite, covellite and chalcocite at different conditions of oxygen partial pressure, temperature and pulp density. Copper extraction increased with temperature, oxygen pressure and agitation speed up to a certain value. They found that vigorous agitation was required to assure a thorough and intimate mixing of oxygen, solution and solids. However, a decrease in copper extraction was continuously observed as the pulp density was increased from a minimum of 5% solids. Improvement in copper extraction was obtained when the oxygen partial pressure was increased. These researchers hinted that when leaching some copper sulphides, oxidation of the copper from the cuprous to cupric state also takes place. Unfortunately they neither gave further details nor pursued the implication of this mode of oxidation in the leaching of copper sulphides. The decrease of copper extraction with increased pulp density, however, is a sign of possible oxygen mass transfer limitation since under mass transfer limitation leaching rates should increase with oxygen partial pressure, mechanical agitation intensity and the area of the gas-liquid interface (Forward and Warren, 1960).

In a study of the total oxidation of Cu$_2$S in sulphate media, Grewal et al. (1992) found that the leaching reactions were kinetically fast. The leaching kinetics was also observed to be sensitive to agitation, which was an indication of possible gas-liquid mass transfer control. It is the intention of this work to investigate the impact of copper (I) oxidation in acidic sulphate media on oxygen mass transfer rates. Metallic copper and cupric sulphate were used as sources of Cu(I) in the presence of sulphuric acid under conditions of total oxidation of chalcopyrite.
2.6 OXIDATION OF COPPER(I) IN AMMONIACAL SULPHATE MEDIA

Although ferric ion is known to oxidize copper sulphides, its very low solubility in ammonia solutions (Forward and Warren, 1960) excludes the possibility of such a reaction. Instead, cupric ions are considered to be the surrogate oxidant acting on the copper sulphides. Cupric ions are produced by the reaction between dissolved oxygen and cuprous ions and this is the gas-liquid reaction of interest for oxygen mass transfer analysis in this system. Peters (1987) proposed such a mechanism, for the leaching of copper sulphides in aqueous ammonia systems. The reaction between dissolved oxygen and cuprous ions in ammonia leaching solution can be represented by the equation:

$$4 \text{Cu(NH}_3\text{)}^+ + \text{O}_2 + n \text{NH}_4\text{OH} \rightarrow 4 \text{Cu(NH}_3\text{)}^{2+} + (n+2)\text{OH}^-$$  Eq. 2-72

The cupric amines ([Cu(NH$_3$)$_n$]$_{n+2}^{2+}$) become the surrogate oxidants for the heterogeneous redox reactions, where they are reduced back to cuprous amine.

This mechanism is supported by experimental data obtained by Beckstead and Miller (1977). In their low pulp density studies they noted that there was a significant effect of the presence of initial cupric ions on the reaction rates. The rate curves for results of experiments carried out without any initial cupric ions displayed a sigmoidal shape. The curves were smoothed by an initial addition of cupric ions that also increased the rate of reaction. The shape of the sigmoidal curves suggests that this reaction was autocatalytic, that is the cupric ions increased the rate of reaction as they were being produced. However, further observation of their results indicates that the reaction rates increased with increase in cupric ion concentration. In order that the catalytic effect be observed, the presence of small quantities of cupric ions is expected to enhance the rate of dissolution but any subsequent increase should not change the rate to a great extent (Hubli et al., 1995).
Therefore, the continued increase of the dissolution rate with increase in cupric ion concentration suggests that cupric amines do not merely catalyze the reaction, but are directly responsible for the leaching process. Although a mere 1% solid density was used in that study, the reaction rate still increased with increase in cupric concentration up to an initial cupric concentration of 30 g/L.

Reilly and Scott (1976) also observed cupric catalysis in their study involving the leaching of chalcopyrite at relatively low pulp densities (7.5 to 30 g solids per liter). They reported an increase in specific rates of reaction with increased pulp density. The increase was accredited to the cupric catalysis. The conclusion was based on the fact that with increase in solids there was an increased possibility of more cupric ions being rapidly dissolved from some fractions of the concentrates such as copper oxides. After complexing with ammonia, the cupric amines would then react with the minerals. Therefore, in practical systems where the leaching is carried out at higher pulp densities, it is unlikely that any effects of cupric ion would be observable. In continuous systems, it is even more difficult to detect the cupric ion factor since the leach system would always contain significant amounts of cupric ion.

Ammonia may complex copper in several forms of both cuprous and cupric complexes in aqueous solution. Cupric ions form the following complexes with ammonia (Bjerrum, 1958):

\[
\text{Cu}^{2+} + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^{2+} \quad K_1 = 4.68 \times 10^3 \quad \text{Eq. 2-73}
\]

\[
\text{Cu(NH}_3\text{)}^{2+} + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^2_2 \quad K_2 = 4.68 \times 10^3 \quad \text{Eq. 2-74}
\]

\[
\text{Cu(NH}_3\text{)}^2_2 + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^2_3 \quad K_3 = 1.10 \times 10^3 \quad \text{Eq. 2-75}
\]

\[
\text{Cu(NH}_3\text{)}^2_3 + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^2_4 \quad K_4 = 1.99 \times 10^2 \quad \text{Eq. 2-76}
\]

\[
\text{Cu(NH}_3\text{)}^2_4 + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^2_5 \quad K_5 = 3.46 \times 10^{-1} \quad \text{Eq. 2-77}
\]
\[
\text{Cu(NH}_3\text{)}^{2+} + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}_6^{2+} \quad K_6 = 2.51 \times 10^{-3} \quad \text{Eq. 2-78}
\]

Cuprous ammonia complexes are as follows:

\[
\text{Cu}^+ + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}^+ \quad K_1 = 8.5 \times 10^5 \quad \text{Eq. 2-79}
\]

\[
\text{Cu(NH}_3\text{)}^+ + \text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}_2^+ \quad K_2 = 8.5 \times 10^4 \quad \text{Eq. 2-80}
\]

The equilibrium constants are given at 25°C. An Eh-pH diagram for the copper-ammonia-water system at 25°C is given in Figure 2-7. In this figure areas of stability for cuprous and cupric amine complexes are shown. Similar stability zones for the respective copper amines are preserved at higher temperatures (up to 100°C) although the stability zone of cupric amines is reduced slightly as temperature is increased. Since both cuprous and cupric amines are stable under typical ammonia leaching conditions, they can take part in the oxidation reaction during pressure leaching in the ammonia system.

The variation in mole fraction of the different cupric amine complexes, as a function of ammonia concentration indicates that when the ammonia concentration is more than 1 molar, the predominant species are the tetramine and pentamine complexes. This relationship is shown in Figure 2-8. A great number of the ammoniacal copper leaching systems use ammonia concentrations in excess of 1 molar.
Figure 2-7  Stability relations of copper compounds presented in an Eh-pH diagram for the Cu-NH$_3$-H$_2$O system at 1 mole per liter total NH$_3$ and activity of copper 0.01M (Burkin, 1966).
Figure 2-8 Copper amine complexes as a function of ammonia concentration at 25°C (Bjerrum, 1941)
The requirements for successful leaching of sulphide minerals of copper, nickel and cobalt in ammonia (Forward, 1953) were found to be the maintenance of a number of chemical and physical conditions. First, sufficient oxygen must be supplied in solution. Second, sufficient ammonia must be supplied to neutralize the acid formed by oxidation of the sulphides, and to form the higher amines of copper, nickel and cobalt together with the amount of unbound ammonia necessary to establish equilibrium with the amines. Third, sufficient anions such as $\text{SO}_4^{2-}$ must be present to convert the copper to soluble ammonia complexes. Fourth, the unbound ammonia should not be so high as to reduce the solubility of the amines. Fifth, the temperature should be high enough for acceptable reaction rates, but not so high as to cause precipitation of basic salts or insoluble complex amines.

In leaching sulphide minerals or concentrates, ammonium sulphate is produced autogenously during the leach to provide the necessary anions (Forward, 1953). Indeed, ammonium sulphate is a byproduct of the ammonia leaching process. However, when leaching a sulphur deficient material such as copper metal, bornite, or chalcocite, it is necessary to provide additional anions in the leach solution, usually by the addition of ammonium sulphate (Forward and Mackiw, 1955). Ammonium sulphate addition was observed to increase the rate of reaction of other pure minerals such as chalcopyrite, or covellite, which have stoichiometrically adequate amounts of sulphur (Stanczyk and Rampacek, 1966). Higher copper extraction and reduced free ammonia requirement are the secondary advantages of adding ammonium sulphate to the leaching solutions.

In the Anaconda Arbiter process (Kuhn et al., 1974) leaching took place at temperatures between 60 and 90°C with oxygen partial pressures of about 5 psig. It was found that leaching kinetics were heavily influenced by oxygen mass transfer and not oxygen partial pressure which is related to oxygen solubility according to Henry’s law. The mass transfer problem was found to lie in the mixing and dispersion of oxygen because when the chemical
reaction rate was made to be the rate controlling mechanism, it was possible to accomplish ammonia leaching in low-pressure systems. Oxygen partial pressure is only important from a kinetic point of view but it is of less importance from a thermodynamic point of view. This fact is indicated in the overall simplified equations below representing the three common copper sulphide minerals. For chalcocite the overall reaction is:

\[
\frac{1}{2} \text{Cu}_2\text{S} + \frac{1}{4} \text{O}_2 + 4 \text{NH}_3 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Cu(NH}_3)_4^{2+} + \frac{1}{2} \text{SO}_4^{2-} + \text{OH}^-
\]

\( \Delta G^0 = -103 \text{ Kcal/mol; } K \approx 10^{75} \ T = 298.15 \ \text{K} \)

For covellite the reaction becomes:

\[
\text{CuS} + 2 \text{O}_2 + 4 \text{NH}_3 \rightarrow \text{Cu(NH}_3)_4^{2+} + \text{SO}_4^{2-}
\]

\( \Delta G^0 = -181 \text{ Kcal/mol; } K \approx 10^{132} \ T = 298.15 \ \text{K} \)

and for chalcopyrite:

\[
\text{CuFeS}_2 + 4 \frac{1}{4} \text{O}_2 + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Cu(NH}_3)_4^{2+} + \frac{1}{2} \text{Fe}_2\text{O}_3 + 2 \text{SO}_4^{2-} + 2 \text{H}^+
\]

\( \Delta G^0 = -374 \text{ Kcal/mol; } K \approx 10^{274} \ T = 298.15 \ \text{K} \)

The large negative standard free energy values confirm that copper sulphide minerals in the presence of aqueous ammonia should be readily attacked.

In the Sherritt Gordon process nickel sulphide is oxidized in ammonia solution through the reaction (Hubli et al., 1995):

\[
\text{NiS} + 2 \text{O}_2 + 6 \text{NH}_3 \rightarrow \text{Ni(NH}_3)_6\text{SO}_4
\]

\( \text{Eq. 2-84} \)

This reaction can also be considered to consist of two parts like those of zinc sulphide pressure leaching. First is the oxidation of nickel sulphide by cupric amine:
\[
\text{NiS} + 8 \text{Cu(NH}_3\text{)}_4^{2+} + 4 \text{H}_2\text{O} \rightarrow \text{Ni(NH}_3\text{)}_6\text{SO}_4 + 8 \text{Cu(NH}_3\text{)}_2^+ + 8 \text{NH}_4^+ + 2 \text{NH}_3
\]

**Eq. 2-85**

Second, the re-oxidation of cuprous amine with dissolved oxygen:

\[
8 \text{Cu(NH}_3\text{)}_2^+ + 2 \text{O}_2 + 8 \text{NH}_4^+ + 8 \text{NH}_3 \rightarrow 8 \text{Cu(NH}_3\text{)}_4^{2+} + 4 \text{H}_2\text{O}
\]

**Eq. 2-86**

Therefore, the gas-liquid reaction here is again the reaction between cuprous amines and oxygen.

However, it was concluded (Kuhn *et al.*, 1974) that one important aspect that was not readily obvious was the rate of oxygen mass transfer. Although oxygen mass transfer into the leaching solution was shown to be of profound importance, it appears that there are no reports in the open literature concerning oxygen mass transfer in ammonia-copper leaching solutions. The objective of the investigation on the copper ammonia system was to attempt to rectify that anomaly.
CHAPTER 3

EXPERIMENTAL PROCEDURES AND EQUIPMENT

The absorption experiments were divided into two categories: experiments performed under surface aeration with a flat interface when the solution was stirred with a single impeller situated at the bottom of the stirrer shaft, and experiments where the solution was agitated vigorously with double impellers. For Fe(II) oxidation under typical zinc pressure leaching conditions, samples were taken at certain time intervals and analyzed whilst the oxidation of Cu(I) was followed by measuring the oxygen consumption using gas mass flowmeters.

3.1 PRELIMINARY EXPERIMENTS

In order to obtain the parameters necessary for the evaluation of the Hatta number, simultaneous observation of mass transfer rates and interfacial area was needed. To fulfill this requirement, the surface characteristics of the solutions used in mass transfer tests were observed as the impeller speed was varied. These preliminary experiments were carried out in a transparent (acrylic) vessel with the same dimensions as the autoclave bomb used in subsequent experiments, but under ambient conditions. In addition to using a transparent vessel with the same dimensions as the autoclave, the same cooling tubes, impeller and impeller shaft and thermocouple well were utilized. Also the stirrer shaft was connected to the same stirring system with its axis rotated on one side of the fixed autoclave heating assembly to give room for the acrylic vessel setup. In short, the head of the autoclave bomb was transferred into the acrylic apparatus before tests were conducted. This way all the geometric dimensions and hydrodynamic characteristics of the autoclave were conserved. Therefore, the differences between these
experiments and those conducted in the autoclave are the high temperature and pressure and the presence of a chemical reaction in the autoclave tests. The objective was to establish the maximum impeller rotation speed at which the liquid surface remained virtually flat. Under the flat interface operation the solution behaves as a quiescent liquid and mass transfer is confined to the free interface; that is mass transfer took place by surface aspiration only. Also it was expected that the maximum possible thinning of the liquid film under a flat interface be obtained under these conditions. The known gas-liquid interfacial area was estimated as equal to the effective mass transfer cross-sectional area of the autoclave bomb (i.e., the internal bomb cross-section minus the area lost to bomb internals). For the mass transfer coefficient, the experimentally measured quantity is usually the volumetric mass transfer coefficient, $k_La$. Since in the flat interface tests the reactor had a fixed transfer area, the variations in $k_La$ reflected those of the true mass transfer coefficient.

With a charge of 1 liter of solution, visual observations indicated that a virtually flat interface between air and the solution could be maintained up to an impeller rotation speed of about 500 rpm. The impeller clearance during these tests was 27 mm in a total solution height of nearly 135 mm. When the impeller speed was increased above 500 rpm, the solution surface became increasingly perturbed, the surface no longer appeared flat, and the area could not be estimated. Such cases were not included in our actual oxidation tests except those used to detect the influence of impeller rotation speed.

Further increase of impeller rotation speed resulted in air bubbles being entrained into the solution. The critical agitation speed required for the surface breakage was also observed visually using the transparent vessel. The agitator speed at which suction of the gas into the solution phase started breaking the vortex was considered as the critical speed, which was found to be about 650 rpm. This was the transition point at which surface convection aeration was clearly observed to change into surface entrainment. The critical
speed has been shown by others (Chaudhari et al., 1987; DeGraaf, 1984) to be a strong function of the position of the impeller. Furthermore, it has been proved that the performance of an impeller for surface aeration is increased when the agitator blades are very near the liquid surface (Hua Wu, 1995). The constant impeller tip speed at which the onset of gas entrainment occurs, for a standard stirred vessel has been correlated independently of the vessel size by Veljkovic and his coworkers (Veljkovic et al., 1991) to be:

\[ N_{cr}D_t = 0.732 \]  

Eq. 3-1

where \( D_t \) is the impeller diameter and \( N_{cr} \) is the critical impeller rotation speed.

At a tip speed below the critical speed and below the value where the surface perturbation occurs, there is a leveling off of interfacial area since agitation intensity no longer affects the area. Therefore, mass transfer tests were conducted at solution stirring speeds which ensured the solution surface was maintained virtually flat and a single impeller was fixed at the bottom of the stirrer shaft.

Tests were also conducted to determine whether the bulk liquid was completely mixed under the flat interface situation. Towards this end, a small amount of anhydrous copper sulphate salt was dropped into the agitated solution and the colour change was observed visually. The copper salt dissolved and the colour of the solution was changed to blue almost instantaneously indicating intensive mixing of the bulk solution at stirrer speeds in excess of 200 rpm.

3.2 FERROUS OXIDATION TESTS UNDER ZINC PRESSURE LEACHING CONDITIONS

The visual observations of the solution surface were complemented by ferrous oxidation tests in the autoclave under zinc pressure leaching conditions to establish the reaction behaviour as impeller speed was varied.
The objective of these tests was to determine the impeller rotation speed that would facilitate maximum ferrous oxidation under flat solution surface conditions and surface aeration. This is similar to testing the microscopic response of the solution surface to variation in impeller rotation speed. The whole range of impeller rotation speeds established in the transparent vessel was repeated here.

Tests were conducted on a 1 litre scale in a standard 2 litre Parr titanium autoclave. Standard 2 litre autoclave bomb has an internal diameter of 102 mm and depth of 267 mm. The autoclave was equipped with a temperature controller, internal vertical cooling tubes also acting as baffles, and a variable speed stirrer system. A single impeller fixed at the bottom of the stirring shaft was used for all tests conducted under the flat interface conditions. An electrically heated jacket assembly surrounding the autoclave bomb provided heating of the autoclave contents. The temperature controller controlled both the heaters in the heating jacket and the cooling water flow. Also the same temperature controller had knobs and a digital speed readout for manual adjustment of the stirrer speed. The temperature of the solution could be controlled to within ±1°C. All wetted parts and the magnetic stirrer were standard and were made of grade 4 titanium. The autoclave head and all valves were made of type 316 stainless steel. The thermocouple well, stirrer and cooling tubes are permanently fixed to the autoclave head.

Agitation was provided by a single 58mm diameter, 45° pitched blade impeller situated at 27 mm above the autoclave bomb bottom for the flat interface and double impeller of the same type for the fully agitated tests. For the double impeller situation, the impeller blades were at 27 mm above the autoclave bottom for the lower impeller and 27 mm below the initial solution level at ambient conditions. All impellers were six bladed and made of titanium. A schematic diagram of the autoclave cross section used for the ferrous oxidation experiments in the flat interface mode is depicted in Figure 3-1.
Figure 3-1 Schematic of the autoclave cross-section illustrating the single impeller position during the flat interface tests
For the ferrous oxidation, synthetic zinc pressure leach solutions were prepared from reagent grade zinc sulphate heptahydrate, ferric sulphate pentahydrate, ferrous sulphate heptahydrate and sulphuric acid. Although ferric sulphate does not take part in the oxidation reaction it was added to provide oxidizing conditions during the solution heating period in order to mimic industrial conditions and to reduce the corrosion of the titanium autoclave. Titanium can be readily corroded at elevated temperatures under reducing conditions (Othmer, 1984; Uhlig, 1971). A standard synthetic leach solution contained 0.2 M FeSO₄, 0.5M H₂SO₄, 2.0 M ZnSO₄ and 0.04M Fe₂(SO₄)₃. An industrial solution obtained from Cominco was also used for some tests. The main constituents of the solution were analyzed and are presented in Table A-I in the Appendix. Make-up sulphuric acid and ferrous sulphate were added to this solution to achieve concentration levels of the synthetic solutions. For a few experiments, the surfactant lignosol was added to the solution prior to the start of the tests. Pure oxygen was supplied from a gas cylinder.

Ferrous oxidation tests were performed on an interruptive basis for two reasons. First, taking samples during an experimental run would have required the removal of solution in the sampling tube so that the sample is representative of the autoclave bulk solution. To accomplish this, oxygen would have to be added through the sampling tube, an action that would have produced bubbles and therefore additional interfacial area, intermittently. In turn, this procedure would vary the total interfacial area haphazardly during the test. Without a known interfacial area, mass transfer rates per unit area could not be determined. Second, the amount of oxygen consumed with the limited flat interface (interfacial area) was too small to be measured by the mass flowmeters, which were available, with any reasonable accuracy.

The interruptive procedure and the use of surface aeration were extended to tests conducted when the autoclave solution was fully agitated with double impellers. The reasons behind this approach were that ferrous
oxidation was fast, with a limited concentration range of interest requiring very short reaction times, and the reaction was very sensitive to variation in oxygen partial pressure. Surface aeration was maintained mainly because oxygen sparging does not provide constant interfacial area for reactions conducted in a batch. In dead end reactors, the reactant gas is supplied to the reactor only to the extent of the consumption and is not sparged at a fixed rate. Hence, interfacial area changes with reaction rate. This situation also exists when laboratory batch autoclave reactors are used (Chaudhari et al., 1985). Surface aeration, however, did not compromise the efficiency of the reactor to mass transfer. At sufficiently high power inputs, there is no difference between the performance of surface aerated and gas sparged vessels. Matsumara et al. (1979) found that for a similar autoclave the difference was insignificant for impeller rotation speeds above 700 rpm.

A typical ferrous oxidation test was performed according to the following sequence. A solution of 1 litre was initially charged to the autoclave bomb. The autoclave bomb was sealed and inserted into the heating assembly. Cooling water tubes, oxygen supply and emergency solution discharge lines were connected. The thermocouple was put in place and the stirrer was connected to the driver system. Heating and slow stirring were initiated and air and vapour were periodically vented up to a solution temperature approaching 100°C. At this temperature the solubility of oxygen is minimum (Kimweri, 1990; Hayduk, 1991). It is, therefore, justifiable to assume that most of the oxygen in the autoclave was in the gaseous phase and venting this gas took out most of the oxygen in the autoclave. When the desired temperature was reached, agitation was increased to the desired speed and then stopped to ensure that oxygen is added to quiescent solution and thus minimize reaction. Oxygen was introduced into the autoclave to a required preset pressure. Switching the stirrer on marked the start of the test. The oxygen overpressure was kept constant at about 709 kPa (7 atm) for most of the tests. Experiments were left to run for 5, 10 or 15 minutes. After each period, stirring was stopped and the autoclave contents were
cooled down, using cold water flowing through the cooling tubes, to about 30°C. The bomb was depressurized and cooling water was shut off. Next, the autoclave bomb was disconnected from the oxygen supply line, the cooling water tubes and the impeller rotating mechanism. The temperature control thermocouple was also removed from its well. After that, the autoclave bomb was taken out of the heating assembly, opened, and a 10 mL sample was taken. To make sure that the solution level in the autoclave remained constant, a volume equal to the sample but of the same concentration as the original solution was added to the autoclave. Changes in solution level could cause a change in the solution hydrodynamics and hence mass transfer characteristics. The autoclave was sealed and another run was started until the total oxidation time was 1 hour. At that point, the volume of the resulting suspension was measured to determine total solution loss. An average of 15 mL was found to be lost through venting, evaporation and other sources. When the interruptive test runs were completed, a single run covering the whole period of one hour was initiated. At the end of the hour, a solution sample was taken for analysis and the ferrous conversion value obtained in this test was used to account for the oxidation that took place during cooling of the interruptive runs.

In the second set experiments were carried out with rotation speeds high enough to enable surface aeration by entrainment of oxygen. A double impeller agitator system was employed for this purpose. The aim of these experiments was either to determine the reaction rate constant and/or to estimate the interfacial area of the fully agitated reactor. A procedure similar to that of the flat interface was followed with few exceptions. First, a lower oxygen partial pressure was used, mostly 20 to 40 psi (137.9 to 275.7 kPa). Second, the impellers were adjusted to higher rotation speeds up to 1200 rpm. Third, the reaction time was limited to two minutes before interruption and sampling. At the end of the interruptive runs a single test was carried out for a time equal to the sum of the times allocated to the interruptive tests. All tests were carried out in duplicate and a third test was conducted in
case the difference between results of the first two tests was larger than 2%. Therefore, the presented data are the averages of two test results.

### 3.3 Analytical Techniques

Solution samples were analyzed for ferrous iron and in some cases for total iron and sulphuric acid. Ferrous iron concentration in the samples was determined by redox titration with a standard (0.1 N) ceric sulphate solution using ferroin ([Fe(phenanthroline)_3]^{2+}) indicator. Since the change in colour at the endpoint (from deep red to colourless or faintly blue) is sudden, an autotitrator was employed to provide a higher degree of accuracy. The titrations were conducted in duplicate and in case of any discrepancy an additional titration was done. The average of the two titration values was the final data.

Total iron was determined by first reducing the ferric content to ferrous iron with granular zinc metal under high acidic conditions and followed by titration with ceric sulphate. The acid content was determined by first reducing all the ferric content in the solution with copper shot after deaeration using nitrogen gas. This was followed by complexing the metals in the solution with Mg-EDTA complex. The resulting solution was then titrated with sodium hydroxide under a nitrogen atmosphere to a preset pH value. The pH value is set for the Mg-EDTA complex solution before the introduction of the sample for which its acid content was determined. Details of the analytical methods have been documented in the literature (Pribil, 1982; Vogel, 1989 and Harris, 1991).

### 3.4 Oxidation of Copper(I) Under Conditions Used for the Total Oxidation of Chalcopyrite in Sulphate Media

The same autoclave described for the iron system was used here. However, some modifications were made to the experimental setup except for the initial tests. The modification involved attaching oxygen mass flowmeters,
which were linked to a computer. This experimental setup is illustrated in Figure 3-2. The connection of the computer to the mass flowmeters enabled the monitoring of the oxygen flow into the reactor, storage of oxygen flow rate data and recognition of the point when the oxidation reaction was complete. Two mass flowmeters in series were used. One had a maximum scale of 2 liters per minute and the second had a maximum scale of 5 liters per minute.

During the initial tests samples were taken from the reactor for analysis of cupric ion content. This operation was also conducted in an interruptive fashion. The concentration of copper in these solution samples was then determined by using atomic absorption spectrometry. Before proceeding with the desired test, a quick check of the impact of stirring speed on oxygen transfer rates for flat interface experiments was undertaken.

While using the mass flowmeters, calibration was found to be necessary at each temperature. The need for calibration arises from the way the autoclave temperature is controlled. As the reaction proceeded, the temperature in the autoclave increased and had to be cooled by running cold water through the cooling tubes. The cooling tubes are exposed above the solution level, cooling the gas and vapour in the space above the solution. When the autoclave contents were cooled, the pressure inside decreased allowing the relatively cool (room temperature) oxygen into the autoclave. Therefore, more oxygen than required for the reaction was introduced into the autoclave. After a while the autoclave contents heated up causing a slight increase in total pressure due to the thermal expansion of oxygen. The successive autoclave cooling cycle therefore, allowed less oxygen than would have otherwise been allowed; hence the need for calibration.
Figure 3-2: Schematic diagram of the autoclave setup with gas mass flowmeters and data acquisition.

Key:

1. Autoclave assembly
2. Oxygen pressurized
3. Valves
4. Magnetic stirrer
5. Solenoid valve
6. Thermocouple
7. Stirrer speed controller
8. Temperature and gas mass flowmeter

Computer

To data acquisition

Computer
The flowmeters were calibrated at each temperature in tests using 10 g of metallic copper in a litre of solution containing 1.0M H₂SO₄ and 0.5M CuSO₄. The resulting solution analyzed for cupric ions by atomic absorption spectrometry. The ratio of the oxygen passed through the flowmeters to the amount that would have been needed for a complete oxidation of the metallic copper gave the calibration factor. In addition to calibration, a blank test, consisting of the same initial solution without added metallic copper, was conducted at each temperature. The amount of oxygen found in the absence of copper reactant was used as a baseline for evaluating the amount of oxygen needed for subsequent tests in which metallic copper was introduced.

In a standard test, the solution was poured into the autoclave bomb followed by the metallic copper. The bomb was then sealed and mounted into the heating assembly. The solution was then heated up to the desired temperature. During heating the autoclave contents were also agitated vigorously to obtain rapid equilibrium. The stirrer rotation speed was kept at the maximum value, about 1200 rpm. Meanwhile, the pressure relief valve was intermittently opened to purge any oxygen entrapped in the bomb. Agitation was continued for about one hour after the desired temperature was reached, in an effort to achieve equilibrium before oxidation was started.

After the equilibration period, the stirrer was stopped and oxygen was added to the desired pressure through the mass flowmeters. The standard oxygen partial pressure for this system was 190 psi. Data acquisition was started. Next, the stirrer was turned on at a preset agitation speed, which marked the beginning of the experimental run. Any subsequent oxygen that flowed into the autoclave was recorded through the mass flowmeters and amounted to the oxygen required for the oxidation of the Cu(I) in the autoclave. The mass flowmeters were used for both the fully agitated autoclave experiments as well as for the experiments conducted under the flat interface mode. In the flat interface mode a single impeller fixed at the bottom of the stirrer shaft was used, whereas in the fully agitated mode a
double impeller arrangement was employed. For the fully agitated tests, agitation speeds above 650 rpm were necessary whilst for the flat interface tests; impeller speeds below 500 rpm were sufficient.

The oxidation of copper was considered to be complete when the mass flowmeters recorded no more oxygen flowing into the reactor. At that point the stirrer was stopped and the oxygen supply was turned off. The set temperature was adjusted to a value equal to the ambient temperature allowing cold water to flow through the cooling tubes. Cooling water flowed through the tubes whenever the set temperature in the temperature controller was adjusted to a value below that of the autoclave contents indicated on the thermocouple readout. When the temperature of the autoclave contents was near room temperature, the bomb was depressurized and opened.

The contents were visually inspected for any residue of copper metal. Solution samples were collected at the end of each experimental run and tested for copper using atomic absorption spectrometry. The atomic absorption spectrometer used for this work was a Unicam 929 model. The wavelength for copper in this machine is 324.8 nm.

Solutions used in these tests were prepared by dissolving technical grade sulphuric acid, cupric sulphate, and ferric sulphate in deionized water. Constant amounts of 1 M H₂SO₄ and 0.072 M Fe₂(SO₄)₃ were maintained for all tests whereas the amount of initial cupric sulphate was varied according to the amount of metallic copper that was to be oxidized. More than stoichiometric amount of cupric ions was provided to set conditions for the metallic copper to disproportionate completely into cuprous ions. However, the method to determine the amount of cuprous ions analytically is so complex (Hahn, 1963) since Cu(I) is not stable at ambient conditions and its amount is a function of the initial solution concentration and temperature.
Experiments were carried out to investigate the effect of oxygen pressure, initial amount of metallic copper, acid concentration and temperature on Cu(I) kinetics or oxygen mass transfer rates.

3.5 OXIDATION OF COPPER(I) IN AMMONIACAL SULPHATE MEDIA

The experimental set up used here is similar to the one explained under the sulphate copper system. The mass flowmeters were used to determine the volume of oxygen that was used in oxidizing a given amount of metallic copper. A calibration exercise similar to the one applied under the sulphate system was also carried out before the flowmeters were used for oxygen flow measurements.

The solutions for all experiments were prepared from analytical grade chemicals. These were ammonium sulphate, ammonia water (ammonium hydroxide) and cupric sulphate. The amount of each chemical was determined by the amount of metallic copper that was to be oxidized. In general, an initial ammonia to total copper mole ratio of 7:1 was used. This amount was recommended to be required for high copper extraction from the study of Tozawa and his coworkers (Tozawa et al., 1976). Ammonium sulphate equivalent to 7/6 times the molar amount of metallic copper was added. Cupric sulphate of about 1.5 times the molar amount of copper metal oxidized was included in the initial solution. The leach solution was prepared by dissolving the specified chemicals in de-ionized water.

In preliminary experiments, the effect of impeller rotation speed on the rate of oxygen consumption in a flat interface mode was determined. Three impeller speeds of 400, 450 and 500 rpm were used. The effects of temperature, oxygen partial pressure, and initial ammonia concentration, as well as initial amount of copper metal were investigated for the fully agitated autoclave.
3.6 SOLUTION VISCOSITY

Solution viscosity was measured using a Brookfield programmable rheometer model DV-III. The viscometer was equipped with an ultra-low viscosity measurement adapter and a corresponding ULA spindle. The ultra-low viscosity adapter was water-jacketed for temperature control. This arrangement enabled the measurement of the viscosities of the different solutions used in this work up to a temperature of about 70°C. Above this temperature, there was excessive loss of water by evaporation. The evaporation of solutions caused a significant change in solution concentration and thus the viscosities measured tended to be larger than expected. In general, solution viscosities decreased with increasing temperature. However, this was not the case at temperatures above 70°C, where measured viscosities appeared to either remain constant or increase slightly due excessive evaporation. Therefore, viscosity measurements were limited to this temperature. A lower temperature limit of 50°C was necessary for the volatile, ammoniacal system.

To obtain viscosity values above 70°C a correlation provided by the Brookfield rheometer manufacturers which is applicable up to 300°C was used:

\[ \mu = A \exp \left( \frac{B}{T} \right) \]

where

\[ B = \left( \frac{T_1 T_2}{T_1 - T_2} \right) \ln \left( \frac{\mu_2}{\mu_1} \right) \]

and

\[ A = \mu_1 \exp \left( \frac{-B}{T_1} \right) \]

Eq. 3-2

In these expressions \( T_1 \) is the temperature at which viscosity \( \mu_1 \) was measured and \( T_2 \) is the temperature at which viscosity \( \mu_2 \) was measured. All temperatures are in Kelvin.

The viscosity of a given solution was measured at two different temperatures \( T_1 \) and \( T_2 \). Viscosity at elevated temperature was then predicted using the relationship above, employing the simultaneous equations.
3.7 SOLUTION DENSITY

Densities of the various solutions used in this work were measured by using 25 ml pycnometers. The pycnometers were calibrated using de-ionized water at all temperatures used in measuring the densities of the solutions. Pycnometers full of solutions were placed into a water bath with a temperature controller capable of maintaining the temperature within ±0.5°C. The water bath was preheated to the required temperature before the pycnometers containing the solutions were placed therein. The pycnometers were placed in such a way that only a few millimeters were left above the water level in the water bath. As the solutions inside the pycnometers expanded, excess solution was allowed to drain through the capillaries drilled through the center of each pycnometer stopper. When sufficient time (about 10 minutes) had been allowed for the temperature of the solution inside the pycnometers to rise to that of the water bath, the pycnometers were withdrawn from the water bath, dried on the exterior and weighed. At a given temperature, the density of each solution was calculated from the expression:

\[ \rho_s = \left( \frac{W_s}{W_w} \right) \rho_w \]  

Eq. 3-3

where \( W_s \) is the solution weight and \( W_w \) is the weight of water. The density of water was obtained from Perry's Chemical Engineers Handbook (Perry et al., 1984). The solution determination using this technique was limited to a maximum temperature of 80°C for all solutions. However, for the most volatile solutions containing ammonia a lower maximum temperature of 50°C was used.

Density values of solutions at higher temperatures were then obtained by either assuming that the thermal expansion of the solution is similar to that of water or by fitting the lower temperature data into a polynomial function followed by extrapolation. These methods were applied for the copper sulphate and copper-ammonia systems. The solution densities for the
zinc pressure leach solutions were measured previously (Kimweri, 1990) and results presented in the form of correlations (Hayduk, 1991). The general correlation for a temperature range between 95 to 185°C is given as:

\[ \rho = \rho_w + 0.637C_{Ac} + 2.162C_{Zn} + 2.536C_{Fe} \]  

Eq. 3-4

Hayduk (1991) also included density correlations at some specific temperatures, which are considered to be more accurate than the general correlation.

3.8 SPECIATION

Since there are no simple methods to determine directly the concentration of cuprous sulphate, cuprous diamine and other species, the concentration of each was obtain via a speciation program. The method is based on the fact that at equilibrium the total Gibbs free energy of the system has its minimum value (Smith and Van Ness, 1975). Therefore, when an expression for the total Gibbs free energy is written the composition that minimizes total Gibbs free energy of the system subject to material balance constraints must be found. The minimum value for the combined material balances and the total Gibbs free energy function then occurs when its partial derivative with respect to the number of each atom type present equals zero. For any single reaction \( k \) at equilibrium, the Gibbs free energy is given by the expression:

\[ \Delta G_k = \Delta G^o_k + RT \ln K_k = 0 \]  

Eq. 3-5

When there is equilibrium between \( j \) species the expression becomes:

\[ \Delta G_k = \sum_j v_{jk} (\Delta G^o_j + RT \ln a_j) \]  

Eq. 3-6

where \( a_j \) is the activity of species \( j \) and \( v_{jk} \) is the stoichiometric factor of species \( j \) in reaction \( k \). By defining Lagrange's unspecified multipliers such that for any species \( j \) composed of elements \( i \):
\[ \Delta G_j^o + RT \ln a_j + \sum_i a_i \lambda_i = 0 \]  \hspace{1cm} \text{Eq. 3-7} \\

where \( a_{ij} \) is the number of elements \( i \) involved in species \( j \), then for all values of \( \lambda_i \):

\[ \sum_k v_{jk} \sum_i a_{ij} \lambda_i = 0 \]  \hspace{1cm} \text{Eq. 3-8} \\

To find a solution, the Gibbs free energy functions must be solved simultaneously for all species \( j \):

\[ \Delta G_j^o + RT \ln a_j + \sum_i a_i \lambda_i = 0 \]  \hspace{1cm} \text{Eq. 3-9} \\

and the set of mole balances for all elements \( i \):

\[ \sum_j a_{ij} m_j = m_i \]  \hspace{1cm} \text{Eq. 3-10} \\

For dissolved species: \( \ln a_j = \ln m_j + \ln \gamma_j \)  \hspace{1cm} \text{Eq. 3-11} \\

For precipitates: \( \ln a_j = 0 \)  \hspace{1cm} \text{Eq. 3-12} \\

Davies' rule has been invoked to calculate the activity coefficient:

\[ -\ln \gamma_j = A_v z_j^2 \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right] \]  \hspace{1cm} \text{Eq. 3-13} \\

where \( A_v \) is the Debye-Huckel coefficient, \( z_j \) is the ionic charge, and \( I \) is ionic strength, defined thus:

\[ I = \frac{1}{2} \sum_j m_j z_j^2 \]  \hspace{1cm} \text{Eq. 3-14} \\

Criss and Cobble heat capacity equations have been used to predict \( \Delta G \) values at elevated temperatures, the detail of which is well documented in the literature (Criss and Cobble, 1964A; Criss and Cobble, 1964B; Cobble, 1964). These same values at 25°C are tabulated in different sources in the literature (Bard et al., 1985; Rossini et al., 1952) and the values used in this work are
presented in Table 3-1. Some data were obtained or calculated using the Outokumpu HSC Chemistry (Version 3.0) software designed for chemical reactions and thermodynamic equilibrium with an extensive thermochemical database.

The results obtained in this work are presented and discussed according to the specific gas-liquid reaction of the desired leaching system. First, results of the oxidation of ferrous iron in synthetic and industrial zinc pressure leach solution from Cominco under zinc pressure leaching conditions are considered. Second, the results concerning the oxidation of Cu(I) in acidic sulphate media under conditions applied in the leaching of chalcopyrite or pyrite are presented. Third, the results obtained when cuprous copper was oxidized in ammoniacal ammonia copper solution under conditions used in the ammonia leaching of copper sulphide concentrates are presented and discussed.
Table 3-1  Thermodynamic data for some species in sulphate and ammonia copper leaching systems

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$, (kJ/mol)</th>
<th>$S^\circ$, (J/K-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\text{a} \text{Cu}$</td>
<td>0.0</td>
<td>33.2</td>
</tr>
<tr>
<td>$^\text{a} \text{Cu}^+$</td>
<td>50.3</td>
<td>41.0</td>
</tr>
<tr>
<td>$^\text{a} \text{Cu}^{2+}$</td>
<td>65.7</td>
<td>-97.2</td>
</tr>
<tr>
<td>$^\text{a} \text{CuSO}_4^0$</td>
<td>-679.1</td>
<td>-79.5</td>
</tr>
<tr>
<td>$^\text{a} \text{CuSO}_4^{aq}$</td>
<td>-679.1</td>
<td>-79.5</td>
</tr>
<tr>
<td>$^\text{a} \text{HSO}_4^-$</td>
<td>-756.0</td>
<td>131.8</td>
</tr>
<tr>
<td>$^\text{a} \text{SO}_4^{2-}$</td>
<td>-744.6</td>
<td>20.1</td>
</tr>
<tr>
<td>$^\text{a} \text{H}^+$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^\text{a} \text{OH}^-$</td>
<td>-157.3</td>
<td>10.2</td>
</tr>
<tr>
<td>$^\text{a} \text{NH}_3$</td>
<td>-26.7</td>
<td>-180.5</td>
</tr>
<tr>
<td>$^\text{a} \text{NH}_4^+$</td>
<td>-79.5</td>
<td>112.8</td>
</tr>
<tr>
<td>$^\text{a} \text{Cu(NH}_3^+)^+$</td>
<td>10.7</td>
<td>81.3</td>
</tr>
<tr>
<td>$^\text{a} \text{Cu(NH}_3)_2^{2+}$</td>
<td>64.6</td>
<td>120.2</td>
</tr>
<tr>
<td>$^\text{a} \text{Cu(NH}_3)^{2+}$</td>
<td>15.9</td>
<td>12</td>
</tr>
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<td>$^\text{a} \text{Cu(NH}_3)_2^{2+}$</td>
<td>-30.6</td>
<td>111.5</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>$^\text{a} \text{Cu(NH}_3)_5^{2+}$</td>
<td>-134.5</td>
<td>330</td>
</tr>
</tbody>
</table>

* Data from Bard et al., (1985)

* Data from Rossini et al., 1952

† Data from Outokumpu HSC Chemistry (Version 3.0) software
The oxidation of Fe(II) under zinc pressure leaching conditions was carried out under a flat interface with a single impeller at the bottom of the stirrer shaft, assuring a known gas-liquid interfacial area. Therefore, oxygen mass transfer rates per unit area could be evaluated. Experimental results concerning the influence of impeller rotation speed on ferrous oxidation in flat interface mode are presented in Figure 4-1 where the ferrous concentration is plotted against time. The plots of results determined at an oxygen partial pressure of 709 kPa and a temperature of 150°C produced straight lines. The slopes of the plots became steeper as the impeller speed was increased up to about 450 rpm. Above this value, the slopes decreased, followed by a nearly constant slope for impeller speeds between 500 to 600 rpm before increasing again at impeller rotation speeds of 650 and 700 rpm. The slopes in this plot represent the ferrous oxidation rates. The straight lines obtained in this figure show that the reaction rate is zero order with respect to ferrous concentration even after oxygen bubbles are entrained in solution stirred by a single impeller at the bottom of the autoclave bomb. From the stoichiometry of the ferrous oxidation reaction, oxygen mass transfer rates were obtained.

A more elaborate presentation of the variation of oxygen mass transfer with agitation speed is as shown in Figure 4-2 where oxygen mass transfer rates are plotted against the impeller rotation speeds at 150°C and an oxygen partial pressure of 709 kPa.
Figure 4-1  \([\text{Fe}^{\text{II}}]\) vs time: effect of stirrer speed under a flat interface at 150°C and 709 kPa oxygen partial pressure using a standard synthetic solution (0.2 M \(\text{FeSO}_4\), 0.5M \(\text{H}_2\text{SO}_4\), 2.0 M \(\text{ZnSO}_4\) and 0.04M \(\text{Fe}_2(\text{SO}_4)_3\))
Figure 4-2 Oxygen mass transfer rate vs stirrer speed under a flat interface at 150°C and 709 kPa oxygen partial pressure using a standard synthetic solution.
The behaviour of the curve shown in Figure 4-2 corresponds to the way a gas is introduced into an agitated liquid during surface aeration. Three distinct regimes of mass transfer from the gas head space to the liquid can be identified in surface aeration depending on the agitation speed and impeller position from the liquid surface (Rossi, 1990). At very low stirring speeds, mass transfer takes place mainly by diffusion and this is referred to as “surface diffusion”. When stirring speed increases and becomes so high that the liquid surface begins to break, convection forces and the rate of surface renewal determine the amount of mass transfer. This regime is called “surface convection”. At higher stirring speeds, liquid surface breakage occurs and the gas is entrained in the liquid. This is called “surface entrainment”. It should be emphasized that there are no clear dividing lines between regimes, and the division of aeration into these regimes depends entirely on the prominence of one mechanism of mass transfer over the others. Therefore, the corresponding mass transfer coefficients generally represent rates that are much greater than those that occur by diffusion alone as a result of the contribution of convection or turbulence at the interface where mass transfer takes place.

It is assumed that the maximum rate of oxygen mass transfer indicated in Figure 4-2 has occurred under the surface diffusion regime based on visual observations at ambient conditions. At impeller rotation speeds below about 400 rpm, the agitation intensity is not strong enough to thin the liquid film sufficiently. Hence, from 0 to 400 rpm the mass transfer rate increases slowly due to increasing diffusion rates with decreasing liquid film thickness and a gradually increasing contribution by surface renewal, though to a small extent. In physical absorption of a gas at ambient temperatures, even slow stirring of the liquid normally has a remarkable effect in reducing the effective thickness of the film (Becker, 1924). This characteristic has been used to promote the absorption of relatively insoluble gases without bubbling the gases through the liquid. However, in the tests conducted during this work,
the oxygen mass transfer rate did not even double over the value obtained at 0 rpm in this range of stirrer speed. This fact may indicate that substantial convection was afforded by the temperature difference under zinc pressure leach conditions in the absence of mechanical agitation. Uniform temperature throughout the solution is only achievable when the solution is sufficiently stirred.

At the stirring speed of 450 rpm, the solution surface was observed to remain virtually flat for tests conducted at ambient conditions. However, at this point the agitation intensity is high enough to thin out the liquid film at the oxygen-solution interface. Since the transfer of reactants takes place mainly by molecular diffusion through the solution film, concentrations of these reactants at the interface are likely to be less than in the bulk solution. However, a notable amount of reactants should also be transferred by surface renewal at this stirring speed. The possible reactants that could be diffusing species are dissolved oxygen, sulphuric acid and ferrous ion. Of interest here is the sulphuric acid concentration. If the acid transfer in the film depends on diffusion and limited surface renewal, then the concentration of acid in the film would be less than that in the bulk solution. The ferrous oxidation reaction significantly increases with decrease in acid concentration (Dreisinger et al., 1990). Other researchers (Baldwin et al., 1995) have correlated the results obtained by the former indicating that the ferrous oxidation rate is proportional to the inverse acid concentration raised to power 0.5. Therefore, the ferrous ions that diffuse to the film from the bulk could be oxidized in a region of low acid concentration. This phenomenon, when coupled with the thinning of the liquid film, gives rise to a higher reaction rate that enhances oxygen mass transfer significantly at a stirrer speed of 450 rpm. Subsequent experiments were carried out at such optimum conditions at every temperature.

Above the stirring speed of 450 rpm, the solution surface characteristics start to be governed predominantly by the surface renewal mode of mass
transfer. Under this mode, sulphuric acid and other reactants are rapidly replenished at the interface as surface solution elements are replaced by other elements from the bulk solution. With higher sulphuric acid concentration at the solution interface, the ferrous oxidation rate decreases markedly.

This effect continues to affect ferrous oxidation even at a stirrer speed above 500 rpm when waves were visually observed to appear on the solution surface at ambient conditions. Above this rotation speed the interface was no longer flat which implies an increase in interfacial area. Yet, the reaction rate was less than that realized at 450 rpm. The phenomenon was only offset by a large increase in interfacial area caused by the entrainment of oxygen bubbles which occurred at an impeller rotation speed of about 650 rpm. At stirring speeds of about 650 rpm, the main oxygen-solution interface was broken by vortex action and bubbles of oxygen were entrained into the bulk solution. Although the entrained oxygen bubbles contributed a small oxygen volume they seem to have provided a larger area for mass transfer compared to the free gas-liquid interfacial area. As can be seen in Figure 4-2, the rate of ferrous oxidation and hence oxygen mass transfer has increased remarkably at an impeller rotation speed of about 700 rpm.

The mass transfer rate against impeller rotation speed indicates that even for the industrial solution as well as the standard synthetic solution with an added 0.3 g/L lignosol, there exists a peak around 450 rpm. The oxygen mass transfer for these solutions and that of the standard solution are presented in Figure 4-3. This maximum mass transfer is not as obvious as for the case of the standard synthetic solution. The reason for this variation might have been the already high mass transfer in the industrial solution before reaching 450 rpm and the relatively low mass transfer for the solution with 0.3 g/L lignosol. Analysis of the industrial solution had shown that it contained some additives such as cupric ions and bismuth, which are known to accelerate the ferrous oxidation reaction. On the other hand the effect of
lignosol in reducing the reaction rate seems to offset the effect produced by rotation speed on the reaction rate. Surfactants tend to produce rigid interfaces and suppress the surface renewal mode of mass transfer (Midoux and Charpentier, 1984). Rigid surfaces might display a very abrupt transition from molecular diffusion to surface renewal mode, which was only detected as a small peak. Also the suppression of surface renewal may lead to the dependence of mass transfer on molecular diffusion alone.

Compared to the rate of reaction in the standard solution the rate for the solution containing 0.3 g/L lignosol was reduced to only about a quarter. The reaction rate in the industrial solution increased by nearly 50% over that in the standard, synthetic zinc pressure leach solution. In general, within the stirrer speed range considered the addition of catalytic additives or that of surfactant lignosol had a stronger effect on the rate of mass transfer than the effect produced by the rotation speed of the impeller.

The effect of the presence of surfactants is better illustrated in Figure 4-4 where the decrease in mass transfer rate with increasing surfactant concentration is clearly shown. Initial addition of 0.1 g/L of lignosol produced a significant reduction in oxygen mass transfer. However, further increase in the amount of lignosol to 0.3 g/L and later to 0.5 g/L caused less additional decrease, which is related to the Fe(II) oxidation reaction. Both findings are in accordance with information from the literature as reviewed in Chapter 2.
Figure 4-3  Oxygen mass transfer rate vs stirrer speed: effect of solution type under a flat interface at 150°C and 709 kPa oxygen partial pressure
Figure 4-4  Effect of surfactant addition on oxygen mass transfer for a standard solution containing various amounts of lignosol, at 150°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
The variation of ferrous concentration with time is depicted in Figure 4-5. From this figure, it can be deduced that the ferrous concentrations seem to decrease linearly with time under the flat interface condition. This is contrary to the findings of most investigators when using a well-agitated tank reactor, including the present work. Typically, second order kinetics are observed with respect to ferrous concentration. Figure 4-5 also shows a slight increase in reaction rate with time; an evidence of autocatalytic tendencies, which have been described above in terms of acid concentration effects. The acid concentration diminished both in bulk solution and at the interface with reaction time.

When different amounts of the initial ferrous concentration were used in the flat interface oxidation tests, results similar to those obtained for the varying temperature were observed as shown in Figure 4-5. All curves were parallel to each other indicating a non-dependence on ferrous concentration on the reaction when tests were conducted in the flat interface mode. The kinetics were close to zeroth order with respect to ferrous concentrations. An exception is noted for the curve representing tests carried out with initial ferrous concentration of 0.1 M. The curve is neither parallel to the others nor straight. As shown below, first order dependence of the reaction on oxygen has been maintained even under the flat interface situation.

The almost straight lines obtained for the Fe(II) concentrations versus time graphs presented in Figure 4-5 and Figure 4-6 show that ferrous oxidation under these conditions is zeroth order with respect to ferrous concentration. Two possible explanations can be advanced with regard to this observation. First, if the actual solubility of Fe(II) at the given test temperature and acid concentration is lower than the amount of Fe(II) initially introduced into the autoclave, then some of the Fe(II) would be tied up as fine precipitates and therefore not available for oxidation.
Figure 4-5  

[Fe(II)] vs time: effect of initial Fe(II) concentration under a flat interface at 150°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed (concentration of other chemicals were similar to the standard synthetic solution)
Figure 4-6  [Fe(II)] vs time: effect of temperature under a flat interface at 709 kPa oxygen partial pressure and 450 rpm stirrer speed using a standard synthetic solution
These precipitates would be acting as a ferrous reservoir being re-dissolved to maintain a constant concentration in the solution as the dissolved Fe(II) was consumed by the oxidation reaction. Since the solutions were allowed to cool down before sampling for analysis, the fine precipitates could be fully re-dissolved prior to chemical analysis. Dreisinger and Peters (1990) reported that precipitates formed in a similar solution at 160°C re-dissolved on cooling to room temperature. It should be pointed out that even in the well-agitated autoclave, a second order reaction rate could not be achieved at concentrations above 0.1 M Fe(II) with the standard solution. The solubility of ferrous sulphate decreases with increase in temperature. In many instances the solubility of ferrous sulphate is on the order of only a few g/L in the temperature range of 150 to 250°C. For example, Jang and Wadsworth (1993) found that the solubility of ferrous pentahydrate (FeSO₄·5H₂O) was only 31.8 g/L (0.13 M) in a 0.27 M H₂SO₄ solution at 200°C. Since the ferrous solubility result was reported for only one temperature, it is not possible to extrapolate this value to other temperatures. Also a further reduction in the ferrous sulphate solubility was expected in solutions used in this work due to the common ion (SO₄²⁻) effect.

Also, due to the small mass transfer area available under the flat interface tests, oxygen mass transfer could limit the reaction rate. However, this proposition was not supported by experimental observation. If the reaction was mass transfer controlled, then based on the Hatta number theory and the established kinetics for ferrous oxidation, which is second order with respect to ferrous concentration, the observed rate of reaction would be expected to be first order with respect to ferrous (Eq. 2-27). Instead, a zeroth order dependence of the reaction on ferrous concentration has been consistently observed. Therefore, mass transfer limitations alone cannot explain the deviation from second order dependence on ferrous concentration as observed experimentally.
4.1 THE INFLUENCE OF TEMPERATURE

The influence of temperature on mass transfer can be explained with reference to Figure 4-6. At temperatures below 140°C the increase in mass transfer with temperature was modest. However, an appreciable increase was noticed at temperatures between 140 and 155°C. This was preceded by a smaller increase in mass transfer at temperatures between 155°C and 160°C. Two factors influence the rate of mass transfer when there is a mass transport process involving a chemical reaction. First is the purely physical mass transfer and second is the rate of chemical reaction. To determine the contribution of each factor, enhancement factors and Hatta numbers were computed at each temperature.

It should be noted that previous investigators managed to achieve acceptable ferrous oxidation rates up to a temperature of 155°C only (Dreisinger and Peters, 1989). When they extended this reaction to 160°C, the rate was found to be very small. Tests conducted at that temperature and impeller rotation speed of 650 rpm produced a white precipitate, which redissolved when the temperature was decreased to ambient conditions. They credited the sharp decrease in ferrous oxidation to a sudden drop in ferrous sulphate solubility. In the present work it was possible to realize relatively rapid ferrous oxidation rates at 160°C by increasing the impeller rotation speed to 1200 rpm. However, the rate decreased dramatically at 165°C. The problem of ferrous solubility was also observed in the flat interface tests at 155 and 160°C when these tests were conducted continuously for one hour using freshly prepared solution. Either using the interruptive procedure or reusing a solution previously used in other ferrous oxidation tests solved the problem. Fresh solutions with ferric concentrations similar to those obtained after complete ferrous oxidation (reused solutions) were tested without any success. The industrial scale reactor being operated continuously provides back mixing of the reactants acting as the reused solution, and the impeller
tip speed is also higher, suggesting that the drop in ferrous solubility might not affect the industrial process at 160°C.

4.2 COPPER CATALYSIS IN THE FLAT INTERFACE MODE

The catalytic role of copper in the oxidation of ferrous iron has been widely documented. The presence of copper in solutions used for ferrous oxidation has been found to increase significantly the rate of reaction. However, all findings were based on experiments conducted in well-stirred reactors. When the reaction was carried out in flat interface mode, the results were mixed as presented in Figure 4-7. Compared to the reaction rate in standard solution without copper, generally the reaction rate increased upon the introduction of copper. At the lower copper concentration (0.0157 M) a higher rate of reaction was obtained. However, when the copper content was further increased to 0.125 M a small reduction was noticed. Yet the reduction was not big enough to approach the rate of ferrous oxidation in the absence of copper. The reduction of the rate can be explained in terms of mass transfer through the flat interface. It has been noted that at 450 rpm optimum conditions exist for the reaction with reference to possible low acid concentration. The addition of copper, catalytic as it is, also increases the electrolyte concentration. Electrolytes tend to produce rigid interfaces suppressing the surface renewal mode and reducing the diffusivity of reactants. Both factors diminish mass transfer rates. Indeed it seems that a further reduction in oxygen mass transfer due to increase in electrolyte concentration was counteracted by the catalytic effect of the added copper. For the lower copper concentration, the effect of copper catalysis far outweighed that of the small increase in electrolyte concentration.
Figure 4-7  [Fe(II)] vs time: effect of cupric addition to the standard synthetic solution under a flat interface at 150°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
4.3 THE EFFECT OF ZINC CONCENTRATION

Another contradictory trend was found on the dependence of ferrous oxidation rate on zinc concentration. Unlike in the fully agitated reactor the results show a decrease in reaction rate with increased zinc concentration in flat interface mode. These results are presented in Figure 4-8. At the lowest zinc concentration of 0.5 M, mass transfer of reactants is least affected by the zinc concentration. However, it is likely that the reaction conditions at the interface were equally favourable. Favourable conditions are represented by a balance between mass transfer by diffusion and surface renewal that produces an environment of lower acid concentration at the interface. When the zinc concentration was increased to 1.0 M a further increase in the reaction rate was observed. However, when the zinc concentration was increased again to 2.0 M a drop in reaction rate was observed due to increased electrolyte concentration hindering mass transfer by surface renewal and convection.

For the first two lower zinc concentrations the plots are curved towards the end indicating high ferrous conversions. It is known that despite the negative effect on mass transfer; electrolytes tend to stabilize smaller gas bubbles in solution, which give higher interfacial area for the same amount of gas compared to large bubbles. As shown below, the reaction rate increased with zinc concentration for tests conducted in the fully agitated reactor where oxygen bubbles were entrained in solution.
Figure 4-8  
[Fe(II)] vs time: effect of zinc concentration under a flat interface at 150°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed using synthetic solution with 0.125 M CuSO$_4$. 
4.4 ENHANCEMENT FACTORS FOR THE FLAT INTERFACE TESTS

Enhancement factors were evaluated from the oxygen mass transfer rates obtained for tests under the flat interface condition. The concentration of oxygen in the bulk solution was assumed to be equal to zero. The basis for this assumption is the fact that the mass transfer is only chemically enhanced when the dissolved gas levels in the bulk are negligible (Astarita, 1967). Hatta number values greater than 3 were obtained for all temperatures as well as for all initial Fe(II) concentrations above 0.1 M used in this work. With the exception of the curve representing Fe(II) oxidation starting with initial Fe(II) concentration of 0.1 M, all the curves are parallel to each other giving an enhancement factor close to that evaluated for the initial concentration of 0.2 M Fe(II) as presented in Table 4-1. Not only was the enhancement value lower than 3 but the curve representing an initial Fe(II) concentration of 0.1 M was not very straight as depicted in Figure 4-5. These changes suggest a basic departure from the conditions existing at the higher ferrous concentrations.

From the Hatta number theory, when the enhancement factor is greater than or equal to 3, the reaction falls under the fast reaction regime and the Hatta number is equal to the enhancement factor, \( H_a = E \), if \( E < E_i \). Results from the calculations are presented in Table I. \( E_i \) was calculated based on the assumption that \( \frac{D_A}{D_B} = 1 \). From this relationship, we can also solve for the intrinsic reaction rate constant:

\[
k = k_m C_B^0 = \frac{1}{D_A} \left( \frac{R}{\partial C_A} \right)^2
\]

Eq. 4-1

From the table a sharp increase in enhancement factor is observed between 140°C and 155°C. This sharp increase is preceded by a decrease in enhancement from 130°C to a minimum value at 140°C. A steady increase is noticed as temperature was increased from 140 to 155°C. This is followed by a decrease in enhancement factor at 160°C. Therefore, although Fe(II) can
be oxidized at a reasonable rate at 160°C under zinc pressure leaching conditions, there is little advantage in terms of the contribution of the reaction rate to the total oxygen mass transfer compared to the temperature of 155°C to warrant increasing the operating temperature. Indeed, the problem of exponential increase in viscosity of the molten sulphur at temperatures in excess of 155°C in the actual industrial zinc pressure leaching process prohibit the use of higher temperatures.

Table 4-I  Enhancement factors under a flat interface at 709 kPa oxygen partial pressure and 450 rpm stirrer speed using a standard synthetic solution

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>R x 10^6 (kmol/m^3s)</th>
<th>R/a x 10^6 (kmol/m^2s)</th>
<th>D_A x 10^9 (m^2/s)</th>
<th>C_A x 10^3 (kmol/m^3)</th>
<th>k_L x 10^5 (m/s)</th>
<th>E_i</th>
<th>E = Ha (-)</th>
<th>k (s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>4.23</td>
<td>0.551</td>
<td>6.21</td>
<td>1.24</td>
<td>5.71</td>
<td>21.1</td>
<td>7.79</td>
<td>31.8</td>
</tr>
<tr>
<td>135</td>
<td>4.53</td>
<td>0.590</td>
<td>6.73</td>
<td>1.35</td>
<td>6.01</td>
<td>19.5</td>
<td>7.29</td>
<td>28.4</td>
</tr>
<tr>
<td>140</td>
<td>4.95</td>
<td>0.646</td>
<td>7.28</td>
<td>1.49</td>
<td>6.32</td>
<td>17.8</td>
<td>6.86</td>
<td>25.8</td>
</tr>
<tr>
<td>145</td>
<td>7.43</td>
<td>0.968</td>
<td>7.86</td>
<td>1.64</td>
<td>6.63</td>
<td>16.2</td>
<td>8.91</td>
<td>44.4</td>
</tr>
<tr>
<td>150</td>
<td>9.07</td>
<td>1.18</td>
<td>8.47</td>
<td>1.80</td>
<td>6.95</td>
<td>14.9</td>
<td>9.45</td>
<td>50.9</td>
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<td>155</td>
<td>11.01</td>
<td>1.44</td>
<td>9.12</td>
<td>1.98</td>
<td>7.28</td>
<td>13.6</td>
<td>9.96</td>
<td>57.6</td>
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<td>160</td>
<td>11.90</td>
<td>1.55</td>
<td>9.81</td>
<td>2.18</td>
<td>7.63</td>
<td>12.5</td>
<td>9.47</td>
<td>53.2</td>
</tr>
</tbody>
</table>
Figure 4-9  Oxygen mass transfer rate vs temperature under a flat interface at 450 rpm and 709 kPa oxygen partial pressure using standard synthetic solution
The results presented in Table 4-I can be interpreted by considering the contribution of the chemical reaction and physical absorption to the oxygen mass transfer. A decrease in the enhancement factor means that the extent by which mass transfer is intensified by the chemical reaction increased at a lower pace compared to that of the physical absorption with temperature. The reverse is true for an increase in enhancement factor with temperature. In this table, the variation of enhancement factor coincides with that of the intrinsic reaction rate constant.

4.5 **OXYGEN MASS TRANSFER AT LOW FERROUS CONCENTRATIONS**

Due to the changes in enhancement factor and the curve shape at a concentration of 0.1 M Fe(II), it was of interest to investigate the behaviour of ferrous oxidation under a flat interface at concentrations below that value. When the initial concentration was reduced to values far below 0.1 M Fe(II), a second order reaction with respect to ferrous was realized under a flat interface. Straight lines were obtained for graphs of inverse Fe(II) versus time for a certain range of Fe(II) concentration. This is what had been obtained when the solutions were fully agitated with double impellers in tests used for kinetic studies, as presented below. The second order test plots for three temperatures are shown in Figure 4-10.

Further ferrous oxidation to higher conversions resulted in negative deviations from the straight plots. Such data are not included in the plots shown in Figure 4-10. Again this is the same behaviour exhibited when ferrous was oxidized in a vigorously agitated reactor. The only difference between the two is that second order behaviour is exhibited at a higher ferrous concentration for tests conducted in a vigorously agitated reactor.
Figure 4-10  Inverse [Fe(II)] vs time at low initial Fe(II) concentrations under a flat interface at 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
4.6 INFLUENCE OF ACID CONCENTRATION AND TRANSITION FROM HIGH TO LOW FERROUS CONCENTRATION

The effect of acid concentration and the transition from high to low Fe(II) concentrations is as presented in Figure 4-11. There is a linear relationship at high concentrations of Fe(II) for the graph of Fe(II) concentration against time. Also, curves are observed at low Fe(II) concentration. When the same data are used to draw a graph of inverse Fe(II) concentration versus time, curves are obtained at high concentrations, which turns into straight lines at low Fe(II) concentration, as already shown for similar data in Figure 4-10.

The effect of acid, which is a reduction in the mass transfer rate is consistent with previous kinetic studies on ferrous oxidation (Dreisinger and Peters, 1990). The same relationship between acid concentration and reaction rate was observed in tests conducted with both high and low initial concentrations of Fe(II). As is notable from Figure 4-11, the effect of acid at concentrations below 0.5M was reversed; that is a further decrease in acid concentration decreased the rate of ferrous oxidation under flat interface operations. One possible explanation is that since at the flat interface the acid was already reduced due to possible mass transfer limitations and the fact that ferrous oxidation requires acid, the acid concentration could have been too low to support the reaction. Indeed when an initial acid concentration of 0.25M was used brownish precipitates were observed. These precipitates could be a result of ferric hydrolysis, which is normally triggered by low acid concentrations. These precipitates could not be redissolved when acid was added to higher concentrations.
Figure 4-11  [Fe(II)] vs time showing the transition from [Fe(II)] above 0.1M to [Fe(II)] below 0.1M and the influence of acid concentration under a flat interface at 150°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed.
4.7 EFFECT OF OXYGEN PARTIAL PRESSURE

The effect of oxygen partial pressure was determined using low Fe(II) concentrations under a flat interface. The results are depicted in Figure 4-12. From the plot, the slopes of the straight lines (which represent the second order rate constant $k_2$) increase with increasing oxygen partial pressure. The logarithm of these slopes is plotted against the logarithm of oxygen partial pressure in Figure 4-13. As expected, the rate is first order with respect to oxygen partial pressure. This is the same finding arrived at by other investigators using well-mixed reactors, and means that constituents other than oxygen are the cause of any differences observed between reactions conducted in well-agitated and flat interface reactors.

4.8 FERROUS OXIDATION IN A WELL-AGITATED REACTOR

With the aim of determining reaction rate constants, experiments were conducted with a dual impeller agitator stirred at high rotation speed, mostly 1200 rpm. The resulting data was tested for second order kinetics at different stirrer speeds, temperatures and initial ferrous concentrations. The experimental results were fitted using the expression:

$$- \frac{d[Fe^{II}]}{dt} = k_{mn}[Fe^{II}]^2C_0$$

Eq. 4-2

Upon integration the following equation is obtained:

$$\frac{1}{[Fe^{II}]_t} = k_{mn}C_0t + \frac{1}{[Fe^{II}]_0}$$

Eq. 4-3

When the inverse ferrous concentrations were plotted against time, straight lines were obtained as reported in previous studies.

Initially, second order curves were plotted for three different stirrer speeds. These plots are shown in Figure 4-14.
Figure 4-12  Inverse [Fe(II)] vs time: effect of oxygen partial pressure under a flat interface at 150°C, 450 rpm stirrer speed and low ferrous concentrations using Cominco’s industrial solution
Figure 4-13  Log-log plot of second order rate constant vs oxygen partial pressure demonstrating first order dependence on oxygen partial pressure
Figure 4-14  Inverse [Fe(II)] vs time: effect of stirrer speed in a well-agitated reactor at 150°C and 138 kPa oxygen partial pressure using standard synthetic solution
By introducing oxygen through surface aeration the gas throughput is a function of the stirring speed. From Figure 4-14 it is obvious that without bubbling oxygen, the stirrer speed of 650 rpm was not strong enough to enable sufficient entrainment and complete dispersion of oxygen in the autoclave. Although two impellers were used in this test, with one placed close to the solution surface, the data obtained at 650 rpm showed no dependence on the ferrous concentration just like those obtained in tests conducted under a flat interface with a single impeller placed at the bottom. At 950 rpm a straight-line with a steeper slope was obtained. When the stirrer speed was increased to 1200 rpm a plot with similar slope to that at 950 rpm resulted. These findings imply that the rotation speed of 950 rpm produced a vigorous enough agitation for complete dispersion of the entrained oxygen bubbles without sparging. However, to ensure complete dispersion of oxygen a stirrer speed of 1200 rpm was used for all subsequent kinetic test runs.

4.8.1 Effect of temperature on the kinetics of ferrous oxidation

Kinetic plots were also made for ferrous oxidation data obtained at temperatures between 130 and 160 °C. Straight lines resulting from the treatment of experimental data are presented in Figure 4-15. These data were also obtained at different oxygen partial pressures. The oxygen partial pressure was 241 kPa at 130°C, 276 kPa at 135°C and 140°C and 138 kPa for temperatures from 145 to 160°C. From these straight lines, the reaction rate constants were calculated at temperatures between 130 and 160°C. These reaction rate constants are presented in Table 4-II. In the same table, reaction rate constants obtained by Dreisinger et al. (1990) under similar conditions were recalculated using oxygen solubility data, which were not available when the investigation by the aforementioned research group was conducted.
Table 4-II  Reaction rate constants at temperatures between 130 and 160°C for standard synthetic solution

<table>
<thead>
<tr>
<th>$T_i$ (°C)</th>
<th>130</th>
<th>135</th>
<th>140</th>
<th>145</th>
<th>150</th>
<th>155</th>
<th>160</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_2$ (m⁶/kmol²-s)</td>
<td>42.5</td>
<td>61.4</td>
<td>94.1</td>
<td>106.7</td>
<td></td>
<td></td>
<td></td>
<td>Dreisinger et al.</td>
</tr>
<tr>
<td>$k_2$ (m⁶/kmol²-s)</td>
<td>41.6</td>
<td>59.4</td>
<td>74.8</td>
<td>81.4</td>
<td>97.6</td>
<td>114.7</td>
<td>144.8</td>
<td>Present work</td>
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</table>

Table 4-III  Reaction rate constants for different solutions at 150°C

<table>
<thead>
<tr>
<th>$k_2$ (m⁶/kmol²-s)</th>
<th>94.1</th>
<th>97.6</th>
<th>123.8</th>
<th>54.2</th>
</tr>
</thead>
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<td>Dreisinger et al.</td>
<td>Present work</td>
<td>Present work</td>
<td>Present work</td>
</tr>
<tr>
<td>Solution</td>
<td>Standard synthetic solution</td>
<td>Standard synthetic solution</td>
<td>Cominco industrial solution</td>
<td>Standard synthetic solution with 0.3 g/L lignosol</td>
</tr>
</tbody>
</table>
Figure 4-15  Inverse [Fe(II)] vs time in a well-agitated reactor at oxygen partial pressures of 241 kPa at 130°C, 276 kPa at 135°C and 140°C, and 138 kPa from 145 to 160°C using standard synthetic solution.
The two studies resulted in reaction rate constants that agree reasonably well with each other considering the two different methods of introducing oxygen into the solution as well as the different impeller rotation speeds. In this study, the dual impeller agitator was rotated at 1200 rpm and oxygen was introduced by surface aeration, whereas in the study by Dreisinger and Peters a speed of 650 rpm was used and oxygen was bubbled into the solution through a dip tube. The present study extended kinetic studies to cover standard solutions with added 0.3 g/L lignosol as well as the industrial solution sample at 150°C. (Kinetic plots for the two solutions are compared with that of the standard solution in Figure B-2 of the Appendix.) Although the small amount of lignosol has no effect on oxygen solubility and solution density (Hayduk, 1991), it caused a significant reduction in the reaction rate constant. For the industrial solution, the strong increase in the reaction rate constant could be attributed to the presence of metallic catalysts such as copper as shown in Table A-I.

*The Influence of initial Fe(II) concentration*

It was also of interest to examine the influence of the initial Fe(II) concentration on the oxidation kinetics. To accomplish this goal solutions containing initial ferrous concentrations between 0.1 M Fe(II) and 0.4 M Fe(II) were prepared and used in kinetic tests at 150°C. The results are illustrated in Figure 4-16.

Two main observations can be made from Figure 4-16. First, all of the resulting curves are almost parallel to each other indicating that the initial ferrous concentration has no influence on the reaction rate constant. Second, all the plots are curved at ferrous concentrations exceeding about 0.1 M Fe(II). This behaviour strongly supports the suggestion that the solubility of ferrous under the conditions covered during this study is in the neighbourhood of 0.1 M. It appears that using ferrous concentrations above this value obscured the true kinetics.
Figure 4-16  Inverse [Fe(II)] vs time: effect of initial ferrous concentration in a well-agitated reactor at 150°C, 138 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 4-17  Inverse [Fe(II)] vs time at 709 kPa oxygen partial pressure and 1200 rpm stirrer speed with 0.0157 M CuSO₄
Many researchers have reported departures from straight lines to curves when high ferrous conversions are realized. A higher oxygen partial pressure and copper catalysis were employed to increase the rate of ferrous oxidation. Results were similarly subjected to the second order test as depicted in Figure 4-17. At low ferrous conversions the plots of inverse ferrous concentration against time are straight lines, but they curve downward at higher ferrous conversions. This negative deviation in slope has also been observed by other investigators (Verbaan and Crundwell, 1986; Iwai et al., 1982). These investigators studied Fe(II) oxidation under different conditions compared to those maintained in the present study. Dreisinger and Peters (1989) reported a positive deviation at ferrous concentrations below 0.02 M for tests conducted under typical zinc pressure leaching conditions similar to those used in this work. Their results corroborated those of other researchers (Huffman and Davidson, 1956) who conducted their investigation under conditions different from those of the zinc pressure leaching process. This behaviour was credited to the prominence of the reaction involving FeSO$_4^0$ neutral species at low ferrous concentrations, which was considered to be faster than that involving the ferrous ion. However, FeSO$_4^0$ was found not to exist at any practically significant level in an elaborate speciation study undertaken by Fillipou and others (Fillipou et al., 1993).
4.9 EFFECT OF ZINC SULPHATE CONCENTRATION

In this work, zinc sulphate was the electrolyte of highest concentration. Its effect on the rate of ferrous concentration was determined by using three solutions with varying zinc sulphate concentrations, keeping the concentrations of Fe(II) and H₂SO₄ constant. The results are illustrated in Figure 4-18. From the figure it can be deduced that ferrous oxidation increased continuously with increase in zinc sulphate concentration. This outcome is in contradiction with what was observed under a flat interface where there was a mixed trend on the effect of the zinc concentration. Maximum ferrous oxidation in that case was realized with 1.0 M zinc in the leach solution. The positive effect of zinc sulphate concentration in the fully agitated reactor tests should be related to the tendency of electrolytes to produce small bubbles, which give larger interfacial areas. This property increases with increasing electrolyte concentration (Mehta and Sharma, 1971). Since the oxygen mass transfer is directly proportional to the interfacial area, increase in interfacial area produces a corresponding increase in reaction rate.

4.10 HATTA NUMBERS FOR THE WELL-AGITATED TESTS

Hatta numbers were determined from the reaction rate constants obtained from the well-agitated reactor tests, using mass transfer coefficients as estimated under a flat interface, calculated oxygen diffusivities, and a ferrous concentration of 0.1 M. This concentration was used because, starting at this concentration, the second order plots were straight and also the previous study (Dreisinger et al., 1990) cited this value as a typical ferrous concentration in the Cominco zinc pressure leach plant. In another source (Baldwin et al., 1995) the typical ferrous concentration in zinc pressure leach solution, as quoted from Cominco staff, was reported to be 0.13 M which is quite close to the former quantity. Values of Hatta numbers at the various
temperatures for an autoclave vigorously agitated by double impellers at 1200 rpm are presented in Figure 4-19 and Table 4-IV.

Table 4-IV  Hatta number vs temperature at 0.1 M Fe(II) and 1200 rpm stirrer speed

<table>
<thead>
<tr>
<th>$T_r$ (°C)</th>
<th>130</th>
<th>135</th>
<th>140</th>
<th>145</th>
<th>150</th>
<th>155</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ha$</td>
<td>0.91</td>
<td>1.08</td>
<td>1.20</td>
<td>1.23</td>
<td>1.35</td>
<td>1.44</td>
<td>1.60</td>
</tr>
</tbody>
</table>

The Hatta number values evaluated for the well-agitated reactor indicate that the ferrous oxidation reaction under these conditions falls in the moderately fast reaction regime. The Hatta number values are greater than 0.3 but lower than 3. Within this range the concentration of oxygen in the bulk solution is very low and the enhancement factor can be greater than 1. It follows that the determination of the reaction rate constant assuming oxygen solubility as the oxygen concentration in the bulk solution may lead to significant errors. From Figure 4-19 and Table 4-IV it is evident that the Hatta number values obtained in a well-agitated reactor are smaller than those under a flat interface as shown in Figure 4-2. The reason behind this difference is related to the autocatalytic tendencies observed under the flat interface tests. These tendencies might have been caused by the possible reduction of the acid concentration in the solution film at the flat interface, which favours a fast ferrous oxidation reaction. Since the residence time of a bubble is small in the relatively small autoclave used in this work, the acid concentration in a bubble film within a well-agitated reactor is not expected to change appreciably. In that case the reaction takes place under relatively high (bulk) acid concentration, hence the autocatalytic advantage is not realized. Actually, the short residence time of the rigid bubbles makes them behave much like the hypothetical fluid elements in surface renewal theory.
Figure 4-18  Inverse [Fe(II)] vs time: effect of zinc concentration in a well-agitated reactor at 150°C, 138 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 4-19  Hatta number vs temperature in the well-agitated autoclave, assuming a 0.1 M Fe(II) effective concentration in the standard synthetic solution
One might anticipate that in the actual commercial zinc pressure leaching plant, small bubbles, which are mostly rigid, are produced. Since the residence time is longer than in the small laboratory scale autoclave, there is a possibility that the acid concentration at the bubble interface could be reduced which in turn would accelerate the rate of ferrous oxidation reaction.

Similar observations have been reported in the autocatalytic oxidation of cyclohexane (Suresh et al., 1988). The investigators found that the mass transfer coefficients observed under a flat interface arrangement were higher than those obtained under a fully stirred reactor. This anomaly was explained in terms of the surface renewal model for the case of the flat interface and rigid bubbles in a well-agitated reactor. However, their observations contradicted this explanation. They observed that in the flat interface, oxygen concentration in the bulk was depleted faster than in the fully stirred reactor and also obtained higher mass transfer coefficients for the flat interface reactor tests. If the flat interface reaction was governed by surface renewal, it would have been expected that more oxygen from the interface would enter the bulk and hence its concentration would be replenished, contrary to their experimental observation. A more fitting explanation would have been the existence of a stagnant film in the flat interface case and bubbles with renewable surfaces under vigorously agitated conditions.

Since the autocatalytic oxidation of cyclohexane produces intermediates which are more reactive than cyclohexane, these intermediates would accumulate faster at the stagnant flat interface than in the bulk. As a result all the oxygen from the plenum would be consumed entirely at the interface and none would reach the bulk. So, as soon as the oxygen that was initially absorbed into the bulk, before the accumulation of the more reactive intermediates at the flat interface, was consumed, the bulk would become depleted of oxygen. Therefore, by the time oxygen was depleted in the bulk of the flat interface reactor, the mass transfer would have already been
enhanced by the fast chemical reaction at the interface. Under such conditions, enhanced mass transfer coefficients were measured instead of the (intended) physical mass transfer coefficients.

In a well-agitated reactor, it takes time for the intermediates to accumulate throughout the reactor because of the uniformity of reactant concentrations brought about by the vigorous agitation, for a sufficiently fast reaction to take place. Due to the small reactor used in their experiments, bubbles had too little time to accumulate intermediates at their interfaces. Further, in a well-agitated reactor, oxygen was continuously added to the bulk through the entrainment of bubbles. The combination of the two actions delayed the depletion of oxygen. The time when the oxygen concentration became negligible in the bulk marked the beginning of enhancement. It is most likely that the tests under vigorously agitated conditions resulted in true, physical mass transfer coefficients. On the contrary, the mass transfer coefficients obtained under a flat interface could have already been enhanced by the rapid chemical reaction at the interface, even before the depletion of oxygen in the bulk. It should be noted that the mode of mass transfer itself could not account for the observed experimental facts. However, the predominance of one mode of mass transfer determined whether the right conditions existed for a fast reaction to take place.

4.11 ACTIVATION ENERGY

An Arrhenius plot illustrating the influence of temperature for the ferrous oxidation reaction between 135 and 160°C is presented in Figure 4-20. The plot resulted in a straight line giving a slope which represents an activation energy of 51.0 kJ/mole, which is well within the reaction controlled regime as found in previous studies. However, this value is nearly 30 kJ/mol below the value reported in the study by Dreisinger et al. (1990) under similar zinc pressure leaching conditions. The main difference is that in the study quoted above, the evaluation of the reaction constants was carried out using a constant partial pressure instead of the oxygen solubility, which is
strongly temperature dependent within the same temperature range. The solubility of oxygen in zinc pressure leaching solutions had not yet been determined at the time when Dreisinger et al (1990) reported their results.

The use of such a procedure amounts to assuming constant oxygen solubility over the considered temperature range, contrary to reality. In the temperature range used for zinc pressure leaching, the solubility of oxygen increases with increasing temperature, as shown in Figure 2-5. Indeed when a constant oxygen solubility was assumed for the results of this study, an Arrhenius plot gave an activation energy of about 79.0 kJ/mol, which is very close to the value obtained by Dreisinger et al. (1990) of 80.0 kJ/mol. As indicated before, the reaction rate constants in the Dreisinger et al. study were recalculated using the calculated oxygen solubility values and presented together with values determined from tests conducted in the present work, in Table 4-II. When these constants were subjected to an Arrhenius plot test, a straight line was obtained and the activation energy of the ferrous oxidation reaction was found to be 55.0 kJ/mol, a value that is comparable to that of 51.0 kJ/mol obtained from the results of the presented work.

Although Verbaan and Crundwell (1982) did not show the oxygen solubility values they employed in their calculations, and given the fact that they conducted their tests at low temperatures (below 100°C), they obtained an activation energy of 68.6 kJ/mol. It is apparent that although the ultimate reaction rate equation obtained by using the oxygen partial pressure (which is equivalent to assuming a constant oxygen solubility at all temperatures) is correct, given the validity of Henry’s law for oxygen saturation, the actual activation energy realized through such a procedure is not.
Figure 4-20  Arrhenius plots for ferrous oxidation in the standard synthetic zinc pressure leach solution
It should be pointed out that there is a fundamental difference between the reaction regime determined by using the activation energy and the one arrived at by using the Hatta number. From the basic theory, the value of the activation energy, which does not depend on reactant concentration, implies that a slow reaction (chemical reaction controlled) remains so even if the concentrations of reactants are increased. Similarly, if the reaction is fast it maintains a fast rate even when there are minute concentrations of reactants. Conversely, the Hatta number value tells us that a reaction limited by chemical reaction at low concentrations of reactants can increase to a level where it can be controlled by mass transfer provided the concentrations of reactants are increased appropriately. Also, the Hatta number theory implies that a fast (mass transfer controlled) reaction can be reduced to a lower rate (chemical reaction controlled) as reactant concentrations are diminished. Therefore, results based on the two theories should not be expected to converge under every circumstance.

4.12 SUMMARY

1. Flat interface tests produced maximum reaction rates at an impeller rotation speed of 450 rpm (1.37 m/s).

2. Fe(II) concentration, above about 0.1 M, had no effect on the reaction rate in flat interface tests and did not obey the second order criteria for the well agitated test results. These results strongly suggest a limitation on Fe(II) solubility in the leach solution.

3. Flat interface results gave Hatta numbers (equal to enhancement factors) higher than 3 at all temperatures and for all concentration above 0.1 M Fe(II).
4. Flat interface test results obeyed second order dependence of the rate on Fe(II) concentration only when the Fe(II) concentration was reduced to values below 0.05M.

5. For surface aeration, a stirrer speed of more than 950 rpm (2.89 m/s) was required for entrainment and thorough dispersion of oxygen.

6. The standard solution with added lignosol (0.3 g/L) produced the least reaction rate and oxygen mass transfer. This implies that the presence of surfactant in the zinc pressure leaching solution has a significant adverse effect to oxygen mass transfer and reaction kinetics.

7. The industrial leach solution from Cominco produced both the maximum reaction rate and oxygen mass transfer when the autoclave was operated either under a flat interface or well agitated.

8. The reaction rate increased with increasing electrolyte concentration under well agitated conditions, but increased and then decreased with electrolyte concentration under a flat interface.

9. Results from the well agitated tests gave Hatta numbers between 0.3 and 3, categorizing the reaction as moderately fast.

10. Hatta numbers increased with increasing temperature for the well agitated test results whereas they increased up to 155°C and then decreased at 160°C under a flat interface.

11. An activation energy of 51.0 kJ/mol was obtained from the well agitated test results, categorizing ferrous oxidation as chemical reaction controlled.

12. There is a contradiction between the results obtained using the activation energy analysis and those obtained from the analysis based on the Hatta number theory.
Before the desired tests were carried out, preliminary experiments were necessary to determine the suitability of using mass flowmeters for measuring oxygen consumption by the Cu(I) oxidation reaction. Flat interface data at 200°C obtained by atomic absorption spectrometry analysis of samples taken every 2 minutes are presented in Figure 5-1 in which the Cu(II) concentrations in g/L are plotted as a function of time. The results indicated that the reaction was fast enough even for test runs conducted under the flat interface reactor arrangement such that mass flowmeters could be used. Also, the reaction rate increased with increasing weight of initial copper metal charge. Therefore, subsequent experiments were followed using mass flowmeters. In all tests oxygen flow rate into the autoclave was measured as the Cu(I) oxidized proceeded.

Since oxygen is responsible for the oxidation of copper to cupric ion, it is fair to assert that the results in Figure 5-1 also indicate an increase in the amount of oxygen consumed and in the rate of consumption of oxygen with an increase in the metallic copper charge. The increments in Cu(II) concentration after metallic copper oxidation correspond to the stoichiometric amount of oxygen consumed.
Figure 5-1  
[Cu(II)] vs time: effect of metallic copper charge under a flat interface at 200°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
Tests for evaluating the effect of temperature, oxygen pressure and the amount of acid on the rate of oxidation of Cu(I) were conducted in a well agitated double impeller autoclave. Plots of the oxygen volume against time did not show a significant effect of the three variables on the reaction. In these tests 10g of metallic copper was charged initially into the reactor for each run, the results of which are presented in Figures 5-2, 5-3 and 5-5.

5.1 EFFECT OF O$_2$ PARTIAL PRESSURE

Figure 5-2 indicates that oxygen pressure in the range used here had no direct relation to the rate of reaction. The reaction rate appears to increase randomly irrespective of the oxygen partial pressure.

5.2 EFFECT OF SULPHURIC ACID CONCENTRATION

As observed from Figure 5-3, there was a slight increase in reaction rate with an increase in initial acid concentration. However, the increase was not significant when compared to the amount of acid increased. It is known that the second dissociation of sulphuric acid (i.e. bisulphate into sulphate and hydrogen ion) is hindered by an increase in temperature and acid concentration. Since the reaction requires acid it was expected that acid would have a more significant positive effect on the reaction. The absence of such behaviour suggests that sufficient acid was already present even when the minimum amount of acid (0.5 M) was used.
Figure 5-2 Oxygen volume vs time in a well-agitated reactor: effect of oxygen partial pressure at 200°C and 1200 rpm stirrer speed
Figure 5-3  Oxygen volume vs time in a well-agitated reactor: effect of acidity at 200°C, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Speciation results indicated that the amount of Cu(I) as a function of the oxygen consumed does not vary with changes in acid concentration. A typical speciation plot is presented in Figure 5-4, which represents the actual concentration predicted at all acid concentrations considered. The speciation results show that at the start of the test there exists a small amount of undissolved metallic copper. Although Cu(I) is oxidized by oxygen, its concentration increases up to the time when all metallic copper has been converted to Cu(I) at which point Cu(I) concentration decreases linearly with the amount oxygen consumed.
Figure 5-4 Speciation results at 200°C and 10 g metallic copper charge in a solution of 1.0 M H$_2$SO$_4$ and 0.5 M CuSO$_4$ (Note that the concentration of CuSO$_4^0$ ion pairs under these conditions is negligible)
5.3 EFFECT OF TEMPERATURE

A small increase in reaction rate was also noted as the temperature was increased. Normally, the rates of chemical reactions tend to increase with temperature. However, the increase in reaction rate as shown in Figure 5-5 does not correspond to the large increase in temperature, say from 180 to 220°C. One of the reasons could be the reduction in hydrogen ion concentration with an increase in temperature. Although the first dissociation of sulphuric acid is normally complete and hence no H$_2$SO$_4$ neutral species exist in solution, the second dissociation is usually incomplete. Furthermore, the degree of the second dissociation of sulphuric acid:

\[ \text{HSO}_4^- \xleftarrow{K_2} \text{H}^+ + \text{SO}_4^{2-} \quad \text{Eq. 5-1} \]

decreases with an increase in temperature, especially above 100°C (Marshall and Jones, 1966, Dickson et al., 1990). The dependence of $K_2$ on temperature (Marshall and Jones, 1966) is given by:

\[ \log K_2 = 56.889 - 19.8858 \log T - 2307.9 T^{-1} - 0.00647 T \quad \text{Eq. 5-2} \]

Since it has already been established that acid has no significant effect on the reaction rate in the concentration range used, the impact of temperature on acid concentration cannot describe the lack of increase in reaction rate with temperature. However, an insignificant effect of temperature on the rate of reaction is a strong indication of mass transfer control.
Figure 5-5  Oxygen volume vs time in a well-agitated reactor: effect of temperature at 10 g metallic copper charge, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Further analysis was attempted to determine the actual impact of temperature on the reaction rate between Cu(I) and O₂. This involved the determination of the concentration of Cu(I) and other species through speciation calculations. The results of speciation calculations depicting the concentration of Cu(I) as a function of temperature are presented in Figure 5-6.

The plots in the figure indicate that with a 10 g metallic copper charge, complete conversion of metallic copper to Cu(I) may be possible only when the temperature is elevated above 220°C. Therefore, all metallic copper did not completely convert to Cu(I) at the beginning of tests conducted at temperatures ranging from 180 to 220°C. Although there was incomplete conversion at all temperatures, once all the metallic copper was dissolved the Cu(I) concentration decreased following the same linear path to completion of the reaction irrespective of the operating temperature.

5.4 EFFECT OF METALLIC COPPER CHARGE

The only variable that was observed to provide a systematic and significant effect was the initial amount of metallic copper charge as shown in Figure 5-7. This figure shows trends similar to those observed when the reaction was followed by determining the amount of Cu(II) depicted in Figure 5-1. The amount of oxygen consumption, and hence its rate increased with an increase in metallic copper charge. Of particular interest are the very similar lengths of time required to complete the reaction for the different copper charges. Also, compared to the oxidation of Fe(II), the oxidation of Cu(I) took a much shorter time, a sign of very fast reaction.
Figure 5-6 Speciation results showing the variation of initial Cu(I) concentration as a function of temperature for 10 g metallic copper charge
Figure 5-7 Oxygen volume vs time in a well-agitated reactor: effect of metallic copper charge at 200°C, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed.
The amount of Cu(I) in the solution was evaluated through speciation calculations, given that the reaction of interest for oxygen mass transfer analysis is one between Cu(I) and oxygen to form Cu(II). In order to evaluate the impact of this reaction to oxygen mass transfer, the concentration of the Cu(I) was required. To achieve that goal, speciation calculations were undertaken. The concentrations of the main species, metallic copper, cupric ion, cuprous ion, fraction oxygen consumed and hydrogen ion as the reaction proceeded, were determined. Typical results of the speciation calculations for the concentration of Cu(I) as a function of initial metallic copper charge for tests conducted at 200°C are depicted in Figure 5-8.
Figure 5-8 Speciation results showing the concentration of Cu(I) as a function of the extent of oxidation at 200°C with 5, 10, 15 and 20 g metallic copper charge
From Figure 5-8, one can see that not all the metallic copper was conproportionated to Cu(I) at the beginning of the experiment except for the initial copper charge of 5 g. Also, the initial concentration of Cu(I) is the same for any metallic copper charge that does not disproportionate completely provided the initial cupric sulphate concentration is the same. When additional cupric sulphate is initially provided a shift in the initial Cu(I) concentration can be expected. Since our interest is the reaction between Cu(I) and oxygen, the analysis of the reaction started at the point where the metallic copper content in the speciation calculations was predicted to be zero. In so doing we intended to avoid dealing with the heterogeneous reaction between metallic copper and Cu(II) to form Cu(I).

The speciation results can be summarized as follows. According to speciation calculations, the concentration of Cu(I) obeys a dual-linear relationship with the extent of oxidation as shown in Figure 5-8. This is because some elemental copper still remains initially in equilibrium with Cu(I) and Cu(II) when the elemental copper charge is in excess of 5g. As long as some elemental copper remains in the system, the ratio of Cu(I) to Cu(II) is fixed by the redox equilibrium, and hence, the concentration of Cu(I) rises linearly with the extent of oxidation. Only after a certain extent of oxidation is the elemental copper fully dissolved, after which point the concentration of Cu(I) falls linearly along the same trajectory as it would have followed had the elemental copper been absent all along.
5.5 HATTA NUMBER ANALYSIS

Raw data were first normalized by scaling to the sum of the stoichiometric amount of oxygen required to complete Cu oxidation plus the calculated oxygen solubility in the respective solutions. Then, a direct numerical differentiation of the experimental data was carried out to obtain rates in terms of oxygen volume at 22.1°C (the calibration temperature of the oxygen mass flowmeters), and the ideal gas law was invoked to convert the rates to moles per unit time. Thus, at time $t_i$ the rate is given as:

$$-r_A = \frac{V_{i+1} - V_{i-1}}{t_{i+1} - t_{i-1}} \left( \frac{p_A}{RT} \right)$$  \hspace{1cm} \text{Eq. 5-3}

A typical plot of reaction rate against time is shown in Figure 5-9. This figure shows three different regions. First is the region of instability where the rates were affected by initial changes in stirrer speed and rapid cooling, and therefore show no systematic relationship with time. The second region depicts stable reaction taking place at high Cu(I) concentration. This is the region of most interest as far as enhancement factors and Hatta numbers are concerned. Third is the region representing oxygen absorption into the bulk solution after most or all of the Cu(I) has been depleted.

Between the second and the third region there is always a point of inflexion. This point is likely to represent the transition from absorption with chemical reaction to a purely physical absorption of oxygen. Therefore, we can assume with confidence that at this point the enhancement factor is almost equal to 1 and the ratio of the rate to the oxygen solubility gives the volumetric mass transfer coefficient $k_{l,a}$ according to equation 2-22. This value was then substituted in the model to find other parameters producing the best fit between model rate values and the experimental results.
Figure 5-9 Oxygen rate vs time in a well-agitated reactor: effect of metallic copper charge at 200°C, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
According to the Hatta number theory, when the Hatta number is high, and the concentration of the dissolved solute is large compared to the saturation concentration of the dissolved gas, then the following relationship applies:

\[- r_A = E k \alpha C_A^* \]  \hspace{1cm} Eq. 5-4

Defining the fraction of oxidation thus:

\[ X_B = \frac{C_b^* - C_B}{C_b^*} \]  \hspace{1cm} Eq. 5-5

\[ \frac{dX_B}{dt} = - \frac{1}{C_b^*} \frac{dC_B}{dt} \]  \hspace{1cm} Eq. 5-6

where \( C_b^* \) is what the initial concentration of Cu(I) would have been had all of the metallic copper charged dissolved initially (equal to twice the quantity of metallic copper charged) according to the reaction, \( Cu^0 + Cu^{2+} \rightarrow 2Cu^+ \).

The rate is then recast in terms of the fraction of oxidation, thus:

\[ \frac{-r_B}{z} = - r_A = \frac{C_b^*}{z} \frac{dX_B}{dt} \]  \hspace{1cm} Eq. 5-7

where \( z \) is the stoichiometric ratio of solute B to gas A.

Applying Porter's explicit enhancement factor correlation, valid for irreversible second order reactions, as modified by Baldi and Sicardi (1975):

\[ E = 1 + (E_i - 1) \left[ 1 - \exp\left( - \frac{(1 + H_a^2)^{1/2} - 1}{E_i - 1} \right) \right] \]  \hspace{1cm} Eq. 5-8

Substituting the expression for \( E_i \) gives:

\[ E_i = 1 + \frac{D_B C_B}{z D_A C_A^*} \]  \hspace{1cm} Eq. 5-9

and also defining the following dimensionless variables and parameters:
\[ \psi = \frac{C_B^a}{C_B^*} \quad \gamma = \frac{D_B}{D_A} \quad \sigma = \frac{C_B^*}{2C_A^*} \]

then the correlation becomes:

\[ E = 1 + \gamma \sigma \psi \left[ 1 - \exp \left( -\frac{(1 + (H a^*)^2 \psi)^{1/2} - 1}{\gamma \sigma \psi} \right) \right] \]  \hspace{1cm} \text{Eq. 5-10}

It can also be shown that:

\[ \frac{dX_B}{dt} = \frac{E k_l a}{\sigma} = -\frac{d\psi}{dt} \]  \hspace{1cm} \text{Eq. 5-11}

After substituting for the expression defining \( E \) above, the final reaction rate equation becomes:

\[ \frac{dX_B}{dt} = \frac{k_l a}{\sigma} \left\{ 1 + \gamma \sigma \psi \left[ 1 - \exp \left( -\frac{(1 + (H a^*)^2 \psi)^{1/2} - 1}{\gamma \sigma \psi} \right) \right] \right\} \]  \hspace{1cm} \text{Eq. 5-12}

And therefore,

\[ -r_A = k_l a C_A^* \left\{ 1 + \gamma \sigma \psi \left[ 1 - \exp \left( -\frac{(1 + (H a^*)^2 \psi)^{1/2} - 1}{\gamma \sigma \psi} \right) \right] \right\} \]  \hspace{1cm} \text{Eq. 5-13}

where

\[ (H a^*)^2 = \frac{D_A k a C_B^*}{k_l^2} = f(T) \text{ at constant } C_B^* \]  \hspace{1cm} \text{Eq. 5-14}

In this expression, \( \gamma \) and \((H a^*/C_B^*)\) are unknown, but assumed to be weak functions of temperature, \( C_A^* \) is known as calculated from the oxygen solubility model put forward by Tromans (1998B), and \( C_B^* \) is known as the maximum possible concentration of Cu(I) if all of the metallic copper were initially completely converted to Cu(I). Furthermore, \( \gamma = 1 - X_B \) and is assumed to be known, and \( k_l a \) may be estimated from the inflexion point between regions II and III.
By assigning different values of $k_\lambda a$ and $Ha$, values of $\sigma$, $\gamma$, and the rate of reaction were computed using an Excel spreadsheet. This exercise was repeated until the values of $Ha$ giving the minimum error between calculated and experimental rates were obtained.

The first parameter of interest is the Hatta number. The variation of the Hatta number with the model prediction is illustrated in Figure 5-10 for a metallic copper charge of 5 g. In this figure the experimental data fit the model curve representing the highest value of the Hatta number. All the Hatta number values that gave the best fit were higher than 3 confirming that the reaction is in the fast reaction regime. Furthermore, the Hatta numbers were higher than the instantaneous enhancement factors, proving that the reaction is well beyond the region where $E = Ha$, and that it can therefore be categorized as an instantaneous reaction. It should be noted that rate values predicted by the model do not change when the Hatta number is increased beyond this value. This is an indication that the Hatta number has no influence on this reaction. Such a situation can only be attained when the reaction is instantaneous because for such reactions, their rates depend entirely on diffusion of the reactants to an extinction plane beyond which the two reactants cannot coexist.

When experimental data were subjected to the same treatment at a different metallic copper charge they fitted well with model values only at high Hatta numbers, once again confirming that an instantaneous reaction took place at all temperatures considered in this work. This is illustrated in Figure 5-11 for the temperature of 200°C where the model fitted very well those rates obtained from experimental data on both sides of the inflexion point at high Hatta numbers. Once more the Hatta number had no influence on the rate of reaction, proving that the reaction was indeed an instantaneous one.
Figure 5-10  Influence of the Hatta number on model fits at 200°C, 5 g metallic copper charge, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 5-11  Influence of the Hatta number on model fits at 200°C, 10 g metallic copper charge, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
From the preceding figures, it is evident that best fits between predicted and experimental rates are only achievable when the Hatta number is high and the reaction is instantaneous. When the Hatta number is also significantly higher than the instantaneous enhancement factor, Porter’s explicit enhancement factor correlation reduces to:

\[ E = E_i \quad \text{Eq. 5-15} \]

When the enhancement factor has reached its limiting value and equals the instantaneous enhancement factor, the rate is given by the equation:

\[ -r_A = E_i k_L a C_A^* \quad \text{Eq. 5-16} \]

By substituting the expression for \( E_i \) then the rate expression becomes:

\[ -r_A = (1 + \gamma \sigma \psi) k_L a C_A^* \quad \text{Eq. 5-17} \]

upon which the final reaction rate equation becomes:

\[ \frac{d\psi}{dt} = -k_L a \frac{(1 + \gamma \sigma \psi)}{\sigma} \quad \text{Eq. 5-18} \]

Separating terms gives:

\[ \int_{1}^{\psi} \frac{d\psi}{1 + \gamma \sigma \psi} = -\frac{k_L a t}{\sigma} \int_{0}^{t} dt \quad \text{Eq. 5-19} \]

which, upon integration, gives:

\[ \psi = \frac{(1 + \gamma \sigma) \exp(-\gamma k_L at) - 1}{\gamma \sigma} \quad \text{Eq. 5-20} \]

When this expression is substituted into the rate equation, the final rate expression becomes:

\[ -r_A = (1 + \gamma \sigma) \exp(-\gamma k_L at) k_L a C_A^* \quad \text{Eq. 5-21} \]

The reaction rate equation 5-21 is valid for a batch reactor, which was the mode the autoclave was operated during the investigation. This
expression defines the reaction rate in region II before the inflexion point. After the inflexion point, in region III, when Cu(I) is depleted and oxygen is physically absorbed to increase its bulk solution concentration, then by a similar analysis the rate of absorption is given as:

\[- r_A = \exp(- k_L a (t - t_i)) k_L a C^*_A \]  

**Eq. 5-22**

where \( t_i \) is the theoretical time required for complete oxidation of Cu(I). The Cu(I) was considered depleted when \( X_B \) was about 0.99. Again, by assigning values of \( \sigma \) and \( k_L a \), values of \( Y \) which gave the global minimum error between calculated and experimental rates were determined using an Excel spreadsheet.

The best fits for different metallic copper charges are presented in Figure 5-12. The model fitted the experimental values very well in both regions II and III. This is another proof that the reaction between Cu(I) and oxygen is an instantaneous one. Model parameters for best fit with experimental results are shown in Table 5-1. From the table it is observed that \( k_L a \) values for the best fit increase with increasing copper charge, which can translate to an increase in the ionic strength of the solution. This trend is supported by the work of Mehta and Sharma (1971) in which \( k_L a \) was found to increase linearly with an increase in the ionic strength of the solution.

**Table 5-I**  
Best fit parameters with metallic copper charge at 200°C and 1200 rpm

<table>
<thead>
<tr>
<th>Cu(^0) charge</th>
<th>5 g</th>
<th>10 g</th>
<th>15 g</th>
<th>20 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_L a, (s^{-1}) )</td>
<td>0.0327</td>
<td>0.0489</td>
<td>0.0751</td>
<td>0.0854</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>5.58</td>
<td>11.23</td>
<td>16.96</td>
<td>23.21</td>
</tr>
<tr>
<td>( Y )</td>
<td>0.396</td>
<td>0.262</td>
<td>0.167</td>
<td>0.136</td>
</tr>
<tr>
<td>( E_i )</td>
<td>3.21</td>
<td>3.95</td>
<td>3.83</td>
<td>4.15</td>
</tr>
</tbody>
</table>
When the modeling was extended to data obtained at different temperatures similar results were obtained. These are presented in Figure 5-13 where best-fit curves are shown for temperatures from 180 to 220°C. Since the instantaneous reaction model fit the data at all temperatures, this is proof that the reaction was indeed an instantaneous reaction. Parameters for which the best fits of the model to experimental results were obtained are presented in Table 5-II, which also indicates that there are moderate, unsystematic changes in $k_La$ with temperature. Factors leading to such behaviour are alluded to in the literature survey in Chapter 2.

Table 5-II  

<table>
<thead>
<tr>
<th>Temperature</th>
<th>180°C</th>
<th>190°C</th>
<th>200°C</th>
<th>210°C</th>
<th>220°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_La$, $(s^{-1})$</td>
<td>0.0621</td>
<td>0.0512</td>
<td>0.0477</td>
<td>0.0478</td>
<td>0.0487</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>13.35</td>
<td>12.26</td>
<td>11.20</td>
<td>10.19</td>
<td>9.22</td>
</tr>
<tr>
<td>$Y$</td>
<td>0.198</td>
<td>0.265</td>
<td>0.333</td>
<td>0.307</td>
<td>0.305</td>
</tr>
<tr>
<td>$E_i$</td>
<td>3.36</td>
<td>4.25</td>
<td>4.73</td>
<td>4.13</td>
<td>3.81</td>
</tr>
</tbody>
</table>
Figure 5-12  Best model fits for different initial metallic copper charges at 220°C, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 5-13  Best model fits for different temperatures at 10 g metallic copper charge, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed
5.6 COPPER(I) OXIDATION UNDER A FLAT INTERFACE

The influence of stirrer speed on the Cu(I) oxidation reaction rate is as illustrated in Figure 5-14. The curves representing oxygen volumes consumed with time for impeller speeds of 400, 450 and 500 rpm are almost overlapping indicating that the reaction is only slightly affected by the stirrer speed in this range. However, a closer observation of the data shows that the amount of oxygen consumed increased slightly with an increase in stirrer speed. For example, the same amount of metallic copper reacted for about 20 seconds longer at 400 rpm than at 450 rpm or 500 rpm. This small change can be explained by the further thinning of the flat interface film at 450 rpm compared to 400 rpm and a slight increase in interfacial area due to perturbation of the solution surface at 500 rpm. Above this stirrer speed the solution surface was no longer flat. Therefore, for consistency, a stirrer speed of 450 rpm was used for all subsequent flat interface tests.

The effect of metallic copper charge followed the same trend under a flat interface as in the well-agitated reactor. The rate of reaction and the volume of oxygen consumed increased with increasing metal charge as illustrated in Figure 5-15.
Figure 5-14 Oxygen volume vs time under a flat interface: effect of stirrer speed at 200°C, 10 g metallic copper charge, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
Figure 5-15  Oxygen volume vs time under a flat interface: effect of metallic copper charge at 200°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed
5.7 ENHANCEMENT FACTORS UNDER A FLAT INTERFACE

Unlike the kinetics of Cu(I) oxidation, which would require a reaction rate constant, the mass transfer rate depends only on interfacial area, oxygen solubility, and the mass transfer coefficient as expressed in equation 2-10. All these parameters could be evaluated whether heterogeneous, homogenous or a combination of these reactions was taking place simultaneously. Therefore, enhancement factors were evaluated despite the indications based on speciation calculations that mixed reactions (heterogeneous and homogeneous) might have taken place. The flat interface data were found to be more appropriate for this purpose because the interfacial area was fixed and known. Experimental data were first fitted to polynomial functions. These functions were then differentiated to obtain the rate of consumption of oxygen by the Cu(I) oxidation reaction in terms of oxygen volume per unit time. The volume rates were converted to moles per second by applying the ideal gas law. The maximum reaction rates found for each metallic copper charge were used in computing the enhancement factor. The solubility of oxygen in solutions of copper and acid containing 4 g/L Fe(III) was estimated by the method proposed by Tromans (1998). One drawback is that Tromans’s procedure does not provide a means to estimate the effect of iron on oxygen solubility. However, considering the small amount of iron relative to that of copper and sulphuric acid, and the fact that most of the iron would precipitate at the temperatures used for total oxidation of copper sulphide, its effect on oxygen solubility was assumed to be negligible. (Oxygen solubility values and their determination method are summarized in Tables A-VIII and A-IX of the Appendix.) From the densities of the solutions measured up to a temperature of 80°C (presented in Table A-V of the Appendix), densities at the operating temperatures were then evaluated by assuming that the solution had a similar thermal expansivity to that of water. The viscosities of the solutions (presented in Table A-VI in the Appendix) were also measured at low temperatures. Viscosity values at elevated temperature, diffusivity and
mass transfer coefficients were obtained using methods outlined above. The resulting enhancement factors based on experimental data and the estimated instantaneous enhancement factor together with other variables are presented in Table 5-III.

Table 5-III   Enhancement factors under a flat interface with metallic copper charge at 200°C, 709 kPa oxygen partial pressure, and 450 rpm stirrer speed (interfacial area $a = 6.67 \text{m}^2/\text{m}^3$)

<table>
<thead>
<tr>
<th>Cu charge (g)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_A \left(10^4 \text{kmol/m}^3\text{-s}\right)$</td>
<td>0.877</td>
<td>1.27</td>
<td>1.33</td>
<td>1.39</td>
<td>1.43</td>
</tr>
<tr>
<td>$k_L \left(10^4 \text{m/s}\right)$</td>
<td>2.14</td>
<td>2.16</td>
<td>2.14</td>
<td>2.17</td>
<td>2.16</td>
</tr>
<tr>
<td>$C_A^* \left(10^3 \text{kmol/m}^3\right)$</td>
<td>8.06</td>
<td>8.19</td>
<td>8.23</td>
<td>8.46</td>
<td>8.56</td>
</tr>
<tr>
<td>$k_L a C_A^* \left(10^5\right)$</td>
<td>1.15</td>
<td>1.18</td>
<td>1.17</td>
<td>1.22</td>
<td>1.25</td>
</tr>
<tr>
<td>$E (-)$</td>
<td>7.6</td>
<td>10.8</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
</tr>
<tr>
<td>$E_i (-)$</td>
<td>5.9</td>
<td>9.8</td>
<td>11.1</td>
<td>13.0</td>
<td>14.5</td>
</tr>
</tbody>
</table>

From the table above, the values of the enhancement factors determined from experimental data are much higher than 3, indicating that the reaction between Cu(I) and oxygen in sulphate media lies within the fast reaction regime. Values of the instantaneous enhancement factor were computed using equation 2-24 by assuming that $D_B = D_A$. The instantaneous enhancement factors $E_i$ presented in Table 5-III are slightly lower than the enhancement factors $E$ obtained experimentally up to a metallic copper charge of 20 g. This is an indication that the reaction was conducted under the instantaneous reaction sub-regime. For the two tests conducted when the initial metallic copper charge was above 20 g the value of the enhancement factors based on experimental results are slightly lower than the instantaneous enhancement factor. This also put the reaction in the very fast reaction regime. Considering the values and methods used to determine both the enhancement factor from experimental results and the instantaneous enhancement factor based on the assumption of equal diffusivity for Cu(I)
and oxygen, one may conclude that for practical purposes, the enhancement factors equal the instantaneous factors. This relationship places the Cu(I) oxidation reaction in the instantaneous reaction sub-regime.

Therefore, the two independent methods used in evaluating the results have both proved that the reaction between Cu(I) and oxygen is an instantaneous reaction, and hence, that it would be impossible to determine the actual reaction rate constants of Cu(I) oxidation under the conditions of the present study.

5.8 SUMMARY

1. Oxygen partial pressure and temperature had very little effect on the rate of Cu(I) oxidation.

2. Speciation calculations indicate that sufficient amounts of Cu(I) and Cu(II) exist under test conditions to take part in the reaction between Cu(I) and oxygen and between Cu(II) and the mineral.

3. Speciation results also indicate that metallic copper conversion to Cu(I) at all temperatures is not complete except for the 5 g metallic copper charge.

4. Flat interface results gave enhancement factors that are, for all practical purposes, equal to the instantaneous enhancement factor.

5. An enhancement factor model at the highest Hatta number fitted results from well-stirred reactor tests very well.

6. The results were fitted very well by an instantaneous enhancement factor model, which corresponds to the enhancement factor model at very high Hatta numbers.

7. The results indicate that the reaction is effectively instantaneous, and that the bulk solution in this system is depleted of oxygen at virtually any Cu(I) concentration.
CHAPTER 6

OXIDATION OF COPPER(I) IN AMMONIACAL SULPHATE MEDIA

Preliminary experiments similar to those conducted in sulphate media indicated that the Cu(I) oxidation reaction consumed sufficient amounts of oxygen to be measured by mass flowmeters, even when the autoclave was operated under a flat interface. The effect of stirrer speed under the flat interface mode is shown in Figure 6-1. This figure shows that the difference in the amount of oxygen consumed as well as its rate for the three stirrer speeds are very small. The small difference when amplified represents a monotonic increase in oxygen consumption rate as the stirrer speed was increased from 400 rpm to 450 rpm and 500 rpm.

Increases in stirrer speed had an effect on the type of gas-liquid interface that was created. Results from the iron system showed that the optimum impeller speed for the film mode was about 450 rpm. The iron system results also supported the visual observations under ambient conditions that at about 500 rpm the surface behaviour shifted from a film model to a surface renewal model. It follows that above the stirrer speed of 500 rpm the reactants were increasingly transported to the reaction interface by convection and below the stirrer rotation speed of 450 rpm the transport of reactants was predominantly by diffusion.

Therefore, for the ammonia-copper system we can deduce that the oxygen consumption rate and hence the Cu(I) oxidation reaction rate increased with an increase in the rate of replenishment of the reactants at the gas-liquid interface. This kind of response is expected for a reaction rate that increases with increasing concentrations of all reactants and which is not autocatalytic. Again, for consistency a stirrer speed of 450 rpm was used for all other flat interface tests.
Figure 6-1  Oxygen volume vs time under a flat interface: effect of stirrer speed at 100°C, 10 g metallic copper charge, and 1310 kPa oxygen partial pressure
6.1 EFFECT OF OXYGEN PRESSURE

Oxygen partial pressure also had a significant effect on the rate of Cu(I) oxidation in the ammonia system. Generally, the rate increased progressively until when the oxygen partial pressure exceeded 800 kPa. Above this oxygen partial pressure the improvement of the reaction rate due to oxygen pressure diminished. The effect of oxygen is depicted Figure 6-2. Beckstead and Miller (1977) reported similar findings. It was reported that at oxygen pressures below 150 kPa the dependence of the reaction rate on oxygen pressure during the oxidative leaching of chalcopyrite in aqueous ammonia was strong and half order with respect to oxygen. However, at higher oxygen pressures the rate of reaction became less dependent on oxygen pressure and approached a reaction order of zero with respect to oxygen. The present results are also supported by the outcome of the study by Tozawa et al. (1976) who found that the chalcopyrite leaching rate at 80°C increased with oxygen pressure up to about 300 kPa and no further benefits were realized when oxygen pressure was increased beyond that value.

Therefore, in subsequent experiments an oxygen partial pressure of 1310 kPa was maintained throughout so that the effect of other factors could be determined free from that of oxygen.

6.2 EFFECT OF METALLIC COPPER CHARGE

Tests were conducted in a well-agitated reactor at metallic copper charges of 5, 10, 15, and 20 g at 100°C and an oxygen partial pressure of 1310 kPa to determine the variation of reaction rate as a function of cuprous amine concentration. As shown in Figure 6-3, it is obvious that the amount of oxygen consumed as well as the rate of Cu(I) oxidation increased with increasing metallic copper charge.
Figure 6-2  Oxygen volume vs time in a well-agitated reactor: effect of oxygen partial pressure at 100°C, 10 g metallic copper charge, and 1200 rpm stirrer speed
Figure 6-3  Oxygen volume vs time in a well-agitated reactor: effect of metallic copper charge at 100°C, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed.
6.3 EFFECT OF TEMPERATURE

Temperatures of 60, 70, 80, 90 and 100°C were used to determine the influence of temperature on the reaction. Generally, the reaction was found to increase slightly with increasing temperature. For these tests the metallic copper charge was kept constant at 10 g and the oxygen partial pressure was 1310 kPa. The same solution composition was maintained at all temperatures. The influence of temperature is depicted in Figure 6-4, which shows that the effect of temperature is small, which in turn suggests the possibility of mass transfer limited reaction.
Figure 6-4  Oxygen volume vs time in a well-agitated reactor: effect of temperature at 10 g metallic copper charge, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed
6.4 SPECIATION RESULTS

The concentrations of cuprous amines corresponding to the different temperatures and metallic copper charges were obtained through speciation calculations. Typical speciation calculation results of the copper amine species are presented in Figure 6-5 for tests conducted at 100°C with a metallic copper charge of 10 g. From the speciation results, the free ammonia concentration was found to be about 1.5 M and the main product of the cuprous diamine oxidation was \( \text{Cu(NH}_3\text{)}_5^{2+} \) as established by Bjerrum (1941). Only minute amounts of \( \text{Cu(NH}_3\text{)}_4^{2+} \) were produced under the experimental conditions used. The figure also indicates that all metallic copper charged (10 g) should have been disproportionated into cuprous amines before the oxidation reaction was initiated.

Speciation results for different metallic copper charges are presented in Figure 6-6 showing the variation of cuprous amine. The results show that cuprous amine concentration increases with increase in metallic copper charge. All charged metallic copper can react with cupric amines to form cuprous amines provided sufficient ammonia, cupric amine and ammonium sulphate is provided. Therefore, cuprous amine concentration decreases linearly with the amount of oxygen consumed for all metallic copper charges. At different temperatures the concentrations of cuprous amines were also deduced from speciation calculations. Since all the metallic copper could react with cupric amine to produce cuprous amines at all temperatures considered, the variation of cuprous amine is the same as that presented for the 10g metallic copper charge at 100°C on Figures 6-5 and 6-6.
Figure 6-5 Speciation results at 100°C, 10 g metallic copper charge and 1.5 M free ammonia
Figure 6-6 Speciation results depicting the effect of metallic copper charge on the concentration of cuprous amine at 100°C
6.5 HATTA NUMBER ANALYSIS

Unlike the sulphate system where elemental copper remains initially for any metallic copper charge in excess of 5 g, all copper is converted mostly to Cu(NH$_3$)$_2$$^+$ for all temperatures and copper charges provided sufficient NH$_3$, SO$_4$$^-$ and Cu(NH$_3$)$_4$$^{2+}$ are present. According to speciation calculations, the concentration of Cu(NH$_3$)$_2$$^+$ follows a linear relationship with the extent of oxidation shown in Figure 6-6.

As in Section 5.3, after the experimental data in oxygen volumes were normalized and numerically differentiated to determine rates, and the rates were converted to moles per unit time by using the ideal gas law.

A representative plot of reaction rate against time is shown in Figure 5-7 for different metallic copper charges. Despite the complete conversion of metallic copper to cuprous amines, three distinct regions still appear similar to the sulphate copper system. First is the region of instability where the rates were affected by initial change in stirrer speed and initial fast heating of the solution and therefore show no systematic relationship with time. In region II an orderly variation of reaction rate with time is observed suggesting a stable reaction. Region III represents oxygen absorption to saturate the solution because most of the cuprous amines have been oxidized. These three regions are also observed when rates at different temperatures are plotted vs time.

The point of inflexion of each curve was used to determine volumetric mass transfer coefficient $k_La$ by assuming that at this point the enhancement factor is almost equal to 1. This value was then substituted in the model to find other parameters producing the best fit between model and experimental rate values.
Figure 6-7  Oxygen rate vs time in a well-stirred reactor: effect of metallic copper charge at 100°C, 1310 psi oxygen partial pressure, and 1200 rpm stirrer speed
Reaction rates determined from models presented in section 5.3 were compared with experimentally determined rates for different values of Ha using an EXCEL spreadsheet until a best fit between the two was obtained. A characteristic best fit is presented in Figure 6-8 where the model prediction and experimentally determined rates converged at the highest Hatta number for a test conducted at 100°C and 190 psi oxygen with a metallic copper charge of 15 g. Hatta numbers above this value did not produce any change in the predicted rate values demonstrating a lack of influence of the Hatta number on the reaction rate. As stated in the previous chapter, this is a proof that the reaction between oxygen and cuprous amines under the conditions employed in this work is instantaneous (Fig. 2.2 f, page 15). The rates of reaction depend entirely on diffusion of the reactants to an extinction plane within the diffusion film.

When experimental data were subjected to the same treatment at a temperature of 60°C, they fitted very well with model values only at highest Hatta number, once again indicating an instantaneous reaction took place at all temperatures considered in this work. This is shown in Figure 6-9 where model rate values fitted very well those rates determined from experimental data on both sides of the inflexion point.

From the preceding figures, one may conclude that model predicted rates and experimental values produce best fits only when the Hatta numbers are very high and the reaction is taken as instantaneous. Therefore, the rest of the experimental data were fitted using an instantaneous reaction model as presented in Section 5.3.

The best fits between model and experimental rates for different metallic copper charges are depicted in Figure 6-10. It is evident that the model fit the data very well on both sides of the inflexion point. Since the model assumes an instantaneous reaction, this is a proof that the reaction between cuprous amines and oxygen under conditions employed in this study is instantaneous.
Figure 6-8 Influence of the Hatta number on model fitting of experimental rates at 100°C, 15 g metallic copper charge, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 6-9  Influence of the Hatta number on model fitting of experimental rates at 60°C, 10 g metallic copper charge, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Figure 6-10  Best model fits of rate data obtained at different metallic copper charges at 100°C, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed
Further observation of Figure 6-10 reveals that the points of inflexion and hence the $k_La$ values presented in Table 6-I for the best fits increases with increasing copper charge, which is equivalent to increased ionic strength. This phenomenon is consistent with the results obtained with the sulphate copper system and concurs with the results reported by Mehta and Sharma (1971) in which $k_La$ was found to increase linearly with increasing ionic strength.

Table 6-I Parameters for best model fits of rate data obtained at different metallic copper charges, 100°C and 1200 rpm

<table>
<thead>
<tr>
<th>Cu° charge</th>
<th>5 g Cu</th>
<th>10 g Cu</th>
<th>15 g Cu</th>
<th>20 g Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_La$, (s^{-1})</td>
<td>0.0311</td>
<td>0.056</td>
<td>0.0821</td>
<td>0.1151</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>4.68</td>
<td>10.63</td>
<td>18.16</td>
<td>26.67</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.485</td>
<td>0.225</td>
<td>0.157</td>
<td>0.112</td>
</tr>
<tr>
<td>$E_i$</td>
<td>3.18</td>
<td>3.39</td>
<td>3.85</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Similar results were obtained at different temperatures as shown in Figure 6-11. Since all experimentally determined rates were fit by the instantaneous reaction rate model values at all temperatures, this is proof that the reaction was indeed instantaneous at all temperatures employed.
Figure 6-11 Best model fits of rate data obtained at different temperatures at 10 g metallic copper charge, 1310 kPa oxygen partial pressure, and 1200 rpm stirrer speed
The parameters for best fit between model and experimental reaction rates are presented in Table 6-II. The table shows no systematic change in $k_{la}$ with temperature. This behaviour is common and has been explained in Chapter 2.

Table 6-II Parameters for best fit between model and experimental results with 10 g metallic copper charge at different temperatures and 1200 rpm

<table>
<thead>
<tr>
<th>Temperature</th>
<th>60°C</th>
<th>70°C</th>
<th>80°C</th>
<th>90°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{la}, (s^{-1})$</td>
<td>0.0500</td>
<td>0.0670</td>
<td>0.0637</td>
<td>0.0698</td>
<td>0.056</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>8.94</td>
<td>9.48</td>
<td>9.96</td>
<td>10.35</td>
<td>10.63</td>
</tr>
<tr>
<td>$Y$</td>
<td>0.246</td>
<td>0.153</td>
<td>0.193</td>
<td>0.167</td>
<td>0.225</td>
</tr>
<tr>
<td>$E_i$</td>
<td>3.20</td>
<td>2.45</td>
<td>2.92</td>
<td>2.92</td>
<td>3.39</td>
</tr>
</tbody>
</table>

It was not the intention of this work to evaluate the volumetric mass transfer ($k_{la}$) of the systems investigated. Therefore, the power consumption, which is required for any modeling of the $k_{la}$ values, was not measured. However, to satisfy the curiosity on their magnitudes, the values presented in Tables 5-I, 5-II, 6-I and 6-II obtained in the two Cu(I) systems are compared with literature values for other systems. It should be mentioned that direct comparison of $k_{la}$ values is only possible for similar electrolyte systems, with the same type, number and position of impellers and at the same conditions. The volumetric mass transfer coefficient is a strong function of ionic strength and type of electrolyte (Mehta and Sharma, 1971). For instance, the dependence of $k_{la}$ on power dissipation in pure liquids is generally less than that found for electrolytes where bubble size is smaller and coalescence is delayed (Bennington, 1997). While a large number
of correlations exist for the case of sparger aeration, very few exist for the the case of surface aeration. Those that exist are for a single disk turbine impeller (Hua Wu, 1995) whereas in this investigation double pitched-blade impellers were used. The disk turbine is a more efficient impeller for gas entrainment and dispersion than the pitched blade impeller. Unlike sparger aeration, in the case of a single disk turbine and surface aeration, $k_La$ values depend on the size and position of the impeller; in other words, the power number is not constant but varies with stirring speed (Hua Wu, 1995). Hence estimation of $k_La$ in the absence of measured values of power consumption is not possible.

Some of the $k_La$ values in the literature are therefore provided for comparison irrespective of the dissimilarities of the systems. Levy et al. (1981) operating at 20°C with a 34 mm diameter four-bladed radial impeller obtained a $k_La$ value of $4.03 \times 10^{-3}$ s$^{-1}$ at 167 rpm in a CO$_2$-distilled water system. In the sodium sulphite oxidation system, a $k_La$ value of $5.67 \times 10^{-3}$ s$^{-1}$ was obtained at 30°C and 500 rpm. These two $k_La$ values are lower than those obtained in the present work. The difference may be due to differences in agitation speed, electrolyte type concentration and composition, and the number and type of impellers used in the two studies.

Bennington and others (1997) obtained a $k_La$ value of 1.3 s$^{-1}$ using a standard two vane pitched rotor of diameter 0.135 m in the sulphite system at 30-35°C and 2590 rpm. Their $k_La$ value is much higher than the values obtained in the current investigation. Impeller type and size, stirring speed, electrolyte concentration and composition could be some of the causes for the difference.

Hua Wu (1995) used a single 0.121 m or 0.183 m six blade disk turbine placed close to the liquid surface, obtained a $k_La$ value of up to 0.25 s$^{-1}$ for stirring speeds above 900 rpm at 25°C. His values are larger than those obtained in the present work. In additional to the difference mentioned for the other investigators, Hua Wu's investigation was conducted with a
catalyst concentration of $10^{-3}$ kmol/m$^3$. This is higher than the $10^{-6}$ kmol/m$^3$ recommended catalyst concentration for determination of $k_L a$ without a chemical enhancement of mass transfer (Bennington et al., 1997; Linek and Vacek, 1981). Therefore, there is a high possibility that the $k_L a$ values obtained in this work were enhanced by the chemical reaction.

Generally, the very different condition ranges covered by other studies found in the literature make the comparison with the present work difficult. However, the $k_L a$ values obtained in this study are within the range of those found in the literature.
6.6 ENHANCEMENT FACTORS UNDER A FLAT INTERFACE

When the metallic copper charge was increased a notable increase in the reaction rate was observed, as shown in Figure 6-12. The smooth curves have the same shape as those produced from the well-agitated reactor tests. Both behaviours indicate that a similar reaction mechanism took place under the flat interface as in the well-agitated reactor because at equilibrium all metallic copper is converted to cuprous amine. This unique outcome is different from the results obtained in the ferrous oxidation tests where there was a difference in the mode of mass transfer and in the oxidation of Cu(I) in the sulphate medium where metallic copper remained suspended in the sulphuric acid-cupric solution at the start of most tests.

Enhancement factors were evaluated for the flat interface test results. Since the gas-liquid interfacial area was kept constant, enhancement factors were computed by first calculating the mass transfer coefficient and oxygen solubility. The reaction rate was determined as the maximum for each metallic copper charge by fitting the experimental data with polynomial functions. These functions were then differentiated to obtain the reaction rates at various oxygen consumption volumes. The liquid side mass transfer coefficient in the solution at operating conditions was calculated using procedures outlined in Chapter 2. (These values are presented in Tables A-X and A-XI of the Appendix.) Oxygen solubility at different temperatures and metallic copper charges was evaluated by the procedure put forward by Tromans (2000) also summarized in chapter 2. The different variables used in the calculation together with the corresponding enhancement factors are shown in Table 6-III. It should be noted that both the mass transfer coefficients and the oxygen solubility decreased with increasing metallic copper charge.
Figure 6-12  Oxygen volume vs time under a flat interface: effect of metallic copper charge at 100°C, 1310 kPa oxygen partial pressure, and 450 rpm stirrer speed
Enhancement factors based on experimentally determined reaction rates were calculated using Equation 2-10 because the specific gas-liquid interfacial area, \( a \), was known to be 7.667 m\(^2\)/m\(^3\) in the flat interface arrangement. The instantaneous enhancement factor was computed by assuming that the ratio of oxygen diffusivity to that of cuprous amine is one.

Table 6-III

Enhancement factors under a flat interface: effect of metallic copper charge at 100°C, 1310 kPa oxygen partial pressure, and 450 rpm stirrer speed

<table>
<thead>
<tr>
<th>Cu(^0) charge</th>
<th>( k_L \times 10^5 ) (m/s)</th>
<th>( R \times 10^5 ) (kmol/m(^2)/s)</th>
<th>( C_A^* ), (kmol/m(^3))</th>
<th>( E ), (-)</th>
<th>( E_i ), (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 g</td>
<td>7.19</td>
<td>6.76</td>
<td>0.0084</td>
<td>16.7</td>
<td>5.7</td>
</tr>
<tr>
<td>10 g</td>
<td>7.03</td>
<td>8.72</td>
<td>0.0074</td>
<td>25.2</td>
<td>11.6</td>
</tr>
<tr>
<td>15 g</td>
<td>6.61</td>
<td>9.4</td>
<td>0.0065</td>
<td>32.6</td>
<td>19.0</td>
</tr>
<tr>
<td>20 g</td>
<td>6.04</td>
<td>9.55</td>
<td>0.0059</td>
<td>40.3</td>
<td>27.7</td>
</tr>
</tbody>
</table>

All enhancement factors evaluated based on the experimental results are higher than the corresponding estimated instantaneous enhancement factors. This fact confirms that the reaction between cuprous amine and oxygen is instantaneous for all metallic copper charges at 100°C. Indeed, the existence of only very small differences between reaction rates at different temperatures indicate that the reaction is instantaneous at all conditions used in this study. The results also confirm that both oxygen and Cu(I) mass transfer limits the oxidation of cuprous amine under the conditions used in this study. Furthermore, for this reaction the solution was depleted of oxygen during the reaction period.
6.7 SUMMARY

1. Changes in temperature and oxygen partial pressure had insignificant influence on the rate of oxidation of Cu(I) in the ammoniacal system.

2. Speciation calculations indicate that sufficient amounts of Cu(I) and Cu(II) exist under test conditions to take part in the reaction between Cu(I) and oxygen and between Cu(II) and the mineral.

3. Speciation results show that all metallic copper is converted to Cu(I) for all copper charges and temperatures considered.

4. Flat interface test results gave enhancement factors that were higher than the instantaneous enhancement factor, indicating that the reaction is effectively instantaneous.

5. An enhancement factor model best fitted the results from the well-stirred reactor tests at the highest Hatta number considered.

6. Since very high Hatta numbers are obtained when the reaction is instantaneous, an instantaneous enhancement factor model was used instead and fitted the results very well.

7. The results indicate that the oxidation of Cu(I) in the ammoniacal leaching system is instantaneous and that the bulk solution is depleted of oxygen at virtually any Cu(I) concentration.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

There does not appear to be any published study which has attempted to investigate oxygen mass transfer in the three oxidative pressure leaching systems considered in this work, under typical leaching conditions. The most common studies reported previously dealt with the rate at which solid mineral particles were being leached, whether they were particles of zinc sulphide or copper sulphide. With the exception of ferrous oxidation there is no evidence that the kinetics of cuprous sulphate or cuprous amine oxidation had been studied as the gas-liquid reactions in the respective leaching systems.

Since the use of available autoclaves was necessary in this study, it was only possible to initiate a beginning of the necessary studies to evaluate fully the extent of usefulness and limitations of this type of approach. In the work done here, we were successful in determining oxygen mass transfer rates per unit interfacial area under a flat interface and under typical operating conditions for the three oxidative pressure-leaching systems.

Further, mass transfer parameter predictions from our study showed that it is possible to determine oxygen mass transfer by using the gas-liquid reactions typically taking place in some hydrometallurgical systems. Additional precise knowledge of oxygen mass transfer processes in electrolytes in the presence of surfactants is needed to give more quantitative predictions. Such studies would appear to be justified from the results of the present work.

From the results, the Hatta numbers and enhancement factors obtained indicate that all solutions are depleted of oxygen at high concentrations of Fe(II) and Cu(I) in both sulphate and ammoniacal media. Hence the use of
oxygen solubility in kinetic equations for these systems appears to be suspect.

The nature of the gas-liquid interface (stagnant film versus surface renewal) has a notable effect on both the kinetics of Fe(II) oxidation and oxygen mass transfer. For example, for Fe(II) oxidation under zinc pressure leaching conditions, a flat interface reactor cannot be used to determine the mass transfer rates of oxygen in a well-agitated laboratory scale autoclave. This is due to the experimental evidence of autocatalytic behaviour in the stagnant film observed in the flat interface tests, a phenomenon that does not exist in a well-agitated laboratory scale autoclave.

In sulphate and ammoniacal media, oxygen mass transfer is enhanced several times over the maximum possible rate of physical absorption under the same conditions under both a flat interface and in a well-agitated reactor. Under typical leaching conditions the reactions between oxygen and Cu(I) are instantaneous in both systems.

It is recommended that, whenever possible, Hatta numbers or enhancement factors should be evaluated for all gas-liquid reactions pertinent to the design and scale-up of hydrometallurgical reactors.

The actual solubility of ferrous sulphate should be determined experimentally under zinc pressure leaching conditions. The determination requires taking samples through a filter fine enough to prevent any fine ferrous precipitates from passing through. The filter should also have sufficient corrosion resistance such that it can remain in solution during the tests since filtration must take place at the test temperature before cooling of the solution, and hence re-dissolving of the ferrous precipitates, takes place.

Since there appears to be a contradiction in applicability between the theory concerning kinetics and the one for mass transfer, efforts should be made to determine the bulk concentration of oxygen under test conditions. If the bulk oxygen concentration is not equal to its solubility, then the use of
oxygen solubility in the kinetic equation is not justifiable and in that case the kinetic equation should be rectified accordingly.

In the course of this study it was realized that there is no data for oxygen solubility in solutions containing Fe(II) simply because of the possible reaction between iron and oxygen. However, many hydrometallurgical systems contain significant amounts of Fe(II) in solution. It is therefore suggested that oxygen solubility be determined in Fe(II) solutions by substituting nitrogen for oxygen.

The Fe(II) oxidation reaction has the potential to enhance oxygen mass transfer in the zinc pressure leaching process. However, higher enhancement factors and Hatta numbers resulted from tests conducted under a flat interface than those conducted in a well-agitated reactor. This implies that there was an autocatalytic behaviour in the former mode of autoclave operation. Therefore, it is not advisable to extrapolate directly from the results obtained using small laboratory batch autoclaves to industrial scale reactors because the reaction rate would tend to increase with the residence time of oxygen bubbles in the reactor.

Results of the present work indicate that the reactions between Fe(II) or Cu(I) and oxygen in the three hydrometallurgical systems studied can be used to determine valuable mass transfer parameters. However, some improvements may be required. First, in the zinc pressure leaching system, it is important to note the effects of copper catalysis, and to make the measurements on industrial solutions. It should be noted that the solution obtained from Cominco produced both the maximum mass transfer rates and the maximum reaction rates whereas copper catalysis produced mixed results. The results obtained when the Cominco solution was used could not be duplicated by any combination of reagent concentration or copper addition to the standard synthetic solution. Second, in the copper sulphate system, the copper sulphate or sulphuric acid concentrations could be increased beyond typical industrial concentrations, as both appeared to aid rapid
production of Cu(I) from the reaction between metallic copper and cupric ion. Third, oxygen partial pressure could be adjusted for both the sulphate and ammoniacal copper systems in such a way that the instantaneous enhancement factor can be increased to a level such that the reactions could fall in the sub-regime of $3 < H_a < E_i/2$. Under this sub-regime, analysis of the results is far simpler than when the reactions fall under the instantaneous sub-regime, as encountered in the present work.
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Stanczyk M.H. and C. Rampacek, 1963, Oxidation Leaching of copper sulphides in acidic pulps at elevated temperatures and pressures, Report of investigations 6193, USBM.

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# APPENDIX A – ADDITIONAL TABLES

Table A-I  Composition of the industrial pregnant solution obtained from Cominco in g/L

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cd</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>H2SO4</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.377</td>
<td>0.201</td>
<td>0.106</td>
<td>8.657</td>
<td>1.687</td>
<td>1.69</td>
<td>37.7</td>
<td>125.9</td>
<td></td>
</tr>
</tbody>
</table>

Table A-II  Viscosity in mPa-s measured for different synthetic zinc pressure leaching solutions at temperatures from 20 to 50°C

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Standard solution</th>
<th>Standard solution + 0.125 M CuSO4</th>
<th>Standard solution + 0.0157 M CuSO4</th>
<th>Solution of 1.0 M ZnSO4 + 0.125 M CuSO4</th>
<th>Solution of 0.5 M ZnSO4 + 0.125 M CuSO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.4</td>
<td>7.3</td>
<td>6.85</td>
<td>4.25</td>
<td>2.95</td>
</tr>
<tr>
<td>25</td>
<td>4.7</td>
<td>6.25</td>
<td>5.9</td>
<td>3.65</td>
<td>2.6</td>
</tr>
<tr>
<td>30</td>
<td>4.2</td>
<td>5.35</td>
<td>5.1</td>
<td>3.25</td>
<td>2.35</td>
</tr>
<tr>
<td>35</td>
<td>3.7</td>
<td>4.65</td>
<td>4.45</td>
<td>2.9</td>
<td>2.15</td>
</tr>
<tr>
<td>40</td>
<td>3.3</td>
<td>4.15</td>
<td>3.95</td>
<td>2.6</td>
<td>1.95</td>
</tr>
<tr>
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<td>3.0</td>
<td>3.7</td>
<td>3.6</td>
<td>2.4</td>
<td>1.8</td>
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<td>2.7</td>
<td>3.3</td>
<td>3.2</td>
<td>2.2</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Table A-III  Density in kg/L measured for different synthetic zinc pressure leaching solutions at temperatures from 25 to 50°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Initial solution composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>0.5 M Zn SO₄, 0.2M FeSO₄, 0.5M H₂SO₄</td>
</tr>
<tr>
<td>25</td>
<td>1.244</td>
</tr>
<tr>
<td>30</td>
<td>1.240</td>
</tr>
<tr>
<td>35</td>
<td>1.238</td>
</tr>
<tr>
<td>40</td>
<td>1.234</td>
</tr>
<tr>
<td>45</td>
<td>1.232</td>
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<tr>
<td>50</td>
<td>1.227</td>
</tr>
<tr>
<td>60</td>
<td>1.219</td>
</tr>
<tr>
<td>70</td>
<td>1.211</td>
</tr>
<tr>
<td>80</td>
<td>1.200</td>
</tr>
</tbody>
</table>
**Table A-IV** Evaluation of reaction rate constants for ferrous oxidation kinetics under zinc pressure leaching conditions, 1200-rpm double impeller vigorously agitated reactor

<table>
<thead>
<tr>
<th>Temp.</th>
<th>165°C</th>
<th>160°C</th>
<th>155°C</th>
<th>150°C</th>
<th>145°C</th>
<th>140°C</th>
<th>135°C</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>20 psi</td>
<td>20 psi</td>
<td>20 psi</td>
<td>20 psi</td>
<td>20 psi</td>
<td>40 psi</td>
<td>40 psi</td>
<td>35 psi</td>
</tr>
<tr>
<td>$C_A^* \times 10^{-4}$</td>
<td>4.78</td>
<td>4.24</td>
<td>3.85</td>
<td>3.5</td>
<td>3.18</td>
<td>5.79</td>
<td>5.27</td>
<td>4.21</td>
</tr>
<tr>
<td>$k_3 C_A^*$</td>
<td>0.0364</td>
<td>0.0614</td>
<td>0.0442</td>
<td>0.0342</td>
<td>0.0259</td>
<td>0.0433</td>
<td>0.0313</td>
<td>0.0175</td>
</tr>
<tr>
<td>$k_3$</td>
<td>76.1</td>
<td>144.8</td>
<td>114.7</td>
<td>97.6</td>
<td>81.4</td>
<td>74.8</td>
<td>59.4</td>
<td>41.6</td>
</tr>
</tbody>
</table>

**Table A-V** Densities of copper sulphate solution containing 4g Fe[III] in kg/L for different initial copper charge

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Copper charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>5 g</td>
</tr>
<tr>
<td>20</td>
<td>1.176</td>
</tr>
<tr>
<td>35</td>
<td>1.167</td>
</tr>
<tr>
<td>50</td>
<td>1.157</td>
</tr>
<tr>
<td>80</td>
<td>1.128</td>
</tr>
</tbody>
</table>
### Table A-VI

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Copper charge 5 g</th>
<th>Copper charge 10 g</th>
<th>Copper charge 15 g</th>
<th>Copper charge 20 g</th>
<th>Copper charge 30 g</th>
<th>Copper charge 40 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.95</td>
<td>2.05</td>
<td>2.05</td>
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<td>2.6</td>
<td>2.75</td>
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<td>1.65</td>
<td>1.75</td>
<td>2.05</td>
<td>2.15</td>
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<tr>
<td>35</td>
<td>1.45</td>
<td>1.5</td>
<td>1.5</td>
<td>1.6</td>
<td>1.85</td>
<td>1.95</td>
</tr>
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<td>50</td>
<td>1.15</td>
<td>1.2</td>
<td>1.2</td>
<td>1.25</td>
<td>1.45</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Viscosities of copper sulphate solution containing 4g Fe[III] in mPa.s for different initial copper charge.
Table A-VII  Solution viscosity and density of copper ammonia solutions after oxidation of 10g metallic copper charge; measured and calculated values

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>20</td>
<td>1011.2</td>
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<td>30</td>
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<td>Measured</td>
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<td>999.6</td>
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<td>70</td>
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<td>80</td>
<td>974.5</td>
<td>Calculated</td>
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<td>90</td>
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<tr>
<td>100</td>
<td>961.0</td>
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<td>0.68</td>
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</tr>
</tbody>
</table>
Table A-VIII  Composition, available water factors and oxygen solubility for sulphuric acid copper solutions containing 14.32 g/L Fe₂(SO₄)₃ and different metallic copper charge

<table>
<thead>
<tr>
<th>$T_r$ °C</th>
<th>Cu charge</th>
<th>$\rho$ at 25°C, kg/L</th>
<th>$f(T)$</th>
<th>Solute</th>
<th>$m_i$, mol/kg H₂O</th>
<th>$\phi$</th>
<th>$\phi_{eff}$</th>
<th>$m_A$ at 1 atm, mol/kg H₂O</th>
<th>$C_A^*$, mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>5 g</td>
<td>1.176</td>
<td>0.001393</td>
<td>CuSO₄</td>
<td>0.591</td>
<td>0.8354</td>
<td>0.7375</td>
<td>0.001027</td>
<td>0.007049</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>H₂SO₄</td>
<td>0.941</td>
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<tr>
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<td>CuSO₄</td>
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<td>0.781</td>
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<td>CuSO₄</td>
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<td>0.000988</td>
<td>0.00678</td>
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<td></td>
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<td>H₂SO₄</td>
<td>0.700</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T$, °C</td>
<td>Cu charge</td>
<td>$\rho$ at 25°C, kg/L</td>
<td>$f(T)$</td>
<td>Solute</td>
<td>$m_i$, mol/kg H$_2$O</td>
<td>$\phi$</td>
<td>$\phi_{\text{eff}}$</td>
<td>$m_A$ at 1 atm, mol/kg H$_2$O</td>
<td>$C_A^*$, mol/L</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>----------------------</td>
<td>--------</td>
<td>--------</td>
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<td>----------------</td>
</tr>
<tr>
<td>180</td>
<td>10 g</td>
<td>1.186</td>
<td>0.001168</td>
<td>CuSO$_4$ H$_2$SO$_4$</td>
<td>0.6682 0.8565</td>
<td>0.8210 0.8476</td>
<td>0.7313</td>
<td>0.000854</td>
<td>0.005893</td>
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<td>1.186</td>
<td>0.001272</td>
<td>CuSO$_4$ H$_2$SO$_4$</td>
<td>0.6682 0.8565</td>
<td>0.8210 0.8476</td>
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<td>0.00093</td>
<td>0.006417</td>
</tr>
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<td>10 g</td>
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<td>0.001393</td>
<td>CuSO$_4$ H$_2$SO$_4$</td>
<td>0.6682 0.8565</td>
<td>0.8210 0.8476</td>
<td>0.7313</td>
<td>0.001019</td>
<td>0.007025</td>
</tr>
<tr>
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<td>0.001532</td>
<td>CuSO$_4$ H$_2$SO$_4$</td>
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Table A-X  Composition, available water factors and oxygen solubility for ammoniacal ammonia copper solutions and different metallic copper charge

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<th>$T$, °C</th>
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<th>$\rho$ at 25°C, kg/L</th>
<th>$f(T)$</th>
<th>Solute</th>
<th>$m_i$, mol/kg H$_2$O</th>
<th>$\phi$</th>
<th>$\phi_{eff}$</th>
<th>$m_A$ at 1 atm, mol/kg H$_2$O</th>
<th>$C_A^*$, mol/L</th>
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Table A-XI  Composition, available water factors and oxygen solubility for ammoniacal ammonia copper solutions at different temperatures

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<th>Solute</th>
<th>$m_i$, mol/kg H$_2$O</th>
<th>$\phi$</th>
<th>$\phi_{air}$</th>
<th>$m_A$ at 1 atm, mol/kg H$_2$O</th>
<th>$C_A^*$, mol/L</th>
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Figure B-1  [Fe(II)] vs time in a reactor with dual impellers: effect of stirrer speed at 150°C and 709 kPa oxygen partial pressure
Figure B-2  Inverse [Fe(II)] in a well-agitated reactor: effect of solution type at 150°C, 709 kPa oxygen partial pressure, and 1200 rpm stirrer speed