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SOLUBILITY OF OXYGEN IN AQUEOUS SULPHURIC ACID-METALLIC SALT  
SOLUTIONS UNDER PRESSURE LEACHING CONDITIONS

by

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Ottawa, Ontario

A thesis submitted to the School of Graduate Studies and  
Research in partial fulfilment of the requirements for  
the degree of  
MASTER OF APPLIED SCIENCE  
in the Department of Chemical Engineering  
University of Ottawa



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## ABSTRACT

The densities and equilibrium solubilities of oxygen were determined in aqueous sulphuric acid containing different amounts of dissolved zinc and ferric sulphate at conditions that simulated the conditions used for pressure leaching of zinc sulphide ores. Measurements of oxygen solubilities were conducted at 368, 398 and 428 K and oxygen partial pressures of 0.4053, 0.7093 and 1.013 MPa. Oxygen partial pressure of 0.2027, 0.4053 and 0.7093 MPa were used at 458 K. Densities of the solutions were also determined at the same conditions.

The equipment for measuring the densities and oxygen solubilities was designed to allow for the severe corrosiveness of the solutions at temperatures above 372 K. A two-stage absorption-desorption process was used in the determination of the oxygen solubilities. The solutions were saturated with oxygen at high temperatures and pressures and then, the volume of gas desorbed at 101.3 kPa and 323 K, was measured. Densities were measured using a density meter at temperatures of 298 and 323 K and by using glass dilatometers at the higher temperatures.

The results for the oxygen solubilities indicate that the solubilities of oxygen in these solutions are closely expressed by Henry's law. The oxygen solubilities were found to be very low, in the order of  $10^{-5}$  mole fraction at an oxygen partial pressure of 101.3 kPa. The addition of the sulphuric acid and the metal salts was found to significantly decrease

the oxygen solubilities. This is equivalent of saying that these electrolytes salt out the oxygen. However, the oxygen solubilities increase with an increase in the partial pressure of oxygen and an increase in temperature. At all temperatures, the densities of these solutions were higher than those of water. Like the density of water, the densities of the solutions decreased with an increase in temperature.

## ACKNOWLEDGEMENT

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## NOMENCLATURE

$a$	Gas activity
$a_A$	Activity of a solvent
$a_B$	Activity of a solute
$A_1$	Cross sectional area of a tube at an initial temperature, $m^2$
$A_{50}$	Cross sectional area of a tube at $50^\circ C$ , $m^2$
$A_T$	Cross sectional area of a tube at a temperature, $T$ , $m^2$
$A_{ZnS}$	Unreacted sulphide surface area, $m^2$
$C_g$	Oxygen solubility, $kg/m^3$ (g/L)
$C_1$	Non-electrolyte solute gas concentration, $kmol/m^3$ (mol/L)
$C_s$	Electrolyte concentration, $kmol/m^3$ (mol/L)
$f$	Fugacity of a gas in a solution, $N/m^2$
$f^0$	Fugacity of a gas in "standard state", $N/m^2$
$K$	Density calibration constant, $kg/m^3$
$k_{g/l}$	Reaction rate constant, gas to liquid, $m^3/s$
$k_1, k_2$	Reaction rate constants, $m^3/s$
$K_H$	Henry's law constant, $N/m^2$
$k_i$	Solute-solute gas interaction parameter, $m^3/kmol$ (L/mol)
$k_s$	Salt effect parameter, $m^3/kmol$ (L/mol)
$k_{sca}$	Setschenow salt effect parameter, $m^3/kmol$

	(L/mol)
$L_{\text{eact}}$	Actual length, m
$L_{\text{eme}}$	Measured length, m
$L_{\text{e1}}$	Length of the solution inside a tube at the initial temperature, m
$L_{\text{eT}}$	Length of the solution inside a tube at a temperature, T, m
$L_{\text{50}}$	Length of the solution inside a tube at a temperature of 50°C, m
$M_{\text{O}_2}$	Molecular weight of oxygen, kg/kmol
$n_{\text{L}}$	Number of moles in 1 m <sup>3</sup> of a solution at 25°C
$p$	Vapour pressure of a solution, Pa (atm, mm Hg)
$P_{\text{A}}$	Partial pressure of a solute, Pa (atm, psi)
$P_{\text{atm}}$	Atmospheric pressure, Pa (atm, psi)
$P^{\circ}$	Vapour pressure of a pure solvent, Pa (atm, psi)
$p_{\text{O}_2}$	Partial pressure of oxygen, Pa (atm, psi)
$P_{\text{v}}$	Operating pressure, Pa (atm)
$r$	Correction factor
$S_{\text{i}}$	Gas solubility in a solution, kmol/m <sup>3</sup> (mol/L)
$S_{\text{i}}^{\circ}$	Gas solubility in a solvent, kmol/m <sup>3</sup> (mol/L)
$T$	Temperature, K
$V$	Volume of liquid at an operating pressure, m <sup>3</sup>
$V_{(\text{g})}$	Volume of gas, m <sup>3</sup> (mL)
$V_{(\text{l})}$	Volume of absorbing solvent, m <sup>3</sup> (mL)

$V_0$	Volume of liquid at 273 K and 101.3 kPa, $m^3$
$x$	Mole fraction
$x_A$	Mole fraction of solvent
$x_B$	Mole fraction of solute

### Greek Symbols

$\alpha$	Bunsen coefficient in a solution
$\alpha^0$	Bunsen coefficient in a pure solvent
$\gamma_A$	Activity coefficient of a solvent
$\gamma_B$	Activity coefficient of a solute
$\gamma_i$	Activity coefficient in a solution
$\gamma_i^0$	Activity coefficient in a pure solvent
$\kappa$	Coefficient of compressibility, $Pa^{-1}$
$\rho_{act}$	Actual density of a solution, $kg/m^3$
$\rho_1$	Density of a solution at an initial temperature, $kg/m^3$
$\rho_E$	Density of ethylene glycol, $kg/m^3$
$\rho_{50}$	Density of a solution at 50°C, $kg/m^3$
$\rho_{me}$	Measured density of a solution, $kg/m^3$
$\rho_T$	Density of a solution at a temperature, T, $kg/m^3$
$\rho_W$	Density of water, $kg/m^3$
$\tau$	Vibrating frequency reading in the density meter
$\tau_E$	Vibrating frequency reading in the density meter for

ethylene glycol

$\tau_w$  Vibrating frequency reading in the density meter for water

### Abbreviations

CANMET Canada Centre for Mineral and Energy Technology  
CIM Canadian Industrial Manufacturers  
IUPAC International Union for Pure and Applied Chemistry

### Others

[ ] Represents concentration, kmol/m<sup>3</sup> (mol/L)  
u/v/w Sulphuric acid in g/L / zinc in g/L / iron in g/L  
Iron Iron as the metal or ferric ion (Fe<sup>3+</sup>)  
Zinc Zinc as the metal or zinc ion (Zn<sup>2+</sup>)

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## 1. INTRODUCTION

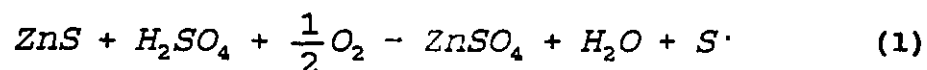
This thesis concerns the measurement of densities and oxygen solubilities in certain aqueous solutions that simulate those found in an actual, new hydrometallurgical process for the recovery of zinc called "pressure leaching". One of the major reasons for the development of the pressure leaching process is that it is a significant innovation in environmental technology. Hence, this thesis is indirectly concerned with the protection of the environment.

In many Canadian ores the metals occur as the metal sulphides. Examples of sulphide ores are those of iron, lead, copper and zinc. Iron may exist as marmatite ((ZnFe)S), pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) or pyrite ( $\text{FeS}_2$ ). Copper is often present in the form of chalcopyrite ( $\text{CuFeS}_2$ ). Normally lead is found as galena ( $\text{PbS}$ ) and zinc as zinc sulphide ( $\text{ZnS}$ ). Of these zinc is of particular importance to Canada, because Canada has the largest estimated zinc reserves in the world (Othmer, 1982a).

The conventional metallurgical method for processing zinc sulphide concentrate is by roasting in air to produce sulphur dioxide and zinc oxide. The product from the roasters which is rich in zinc oxide, is then reacted with sulphuric acid to form zinc sulphate in an acid leach step. The sulphate is purified by using convectional methods and then sent for electrowinning to recover the zinc. Usually, the hot gases

containing sulphur dioxide (SO<sub>2</sub>) from the roasting operation are partially cooled and used in the production of sulphuric acid. Most of the sulphur dioxide is scrubbed from the effluent gases before they are released to the atmosphere, but the scrubbing is not complete. The residual sulphur dioxide is the major source of acid rain (Leaf, 1990). Even with double absorption (double-contact) sulphuric acid plants, the maximum sulphur dioxide removal efficiency from the effluent gases is 99.8%, (Othmer, 1982b). The sulphur dioxide remaining is still a major source of atmospheric pollution.

The new pressure leaching process uses pure oxygen and low concentrations of sulphuric acid, at high temperature and pressure (to 458 K and 2.0 MPa). Pressure leaching directly converts zinc sulphide into zinc sulphate and elemental sulphur. The overall reaction is as follows:



This single reaction step replaces the two reactions that were essential in the conventional processing method. The pressure leaching process used to recover zinc has been under development by Sherrit Gordon Mines of Toronto since 1957. The licensing rights to this new technology are owned by Sherrit Gordon Mines. This process has been applied commercially by Cominco at Trail where a pressure leaching plant with a capacity to process 190 t/d of zinc concentrate

started operating in January 1981. Another plant designed to treat 105 t/d of zinc concentrate started operation at the zinc plant of Kidd Creek Mines at Timmins, Ontario. Both plants were integrated with existing facilities which utilized the roast-leach process. Other Canadian companies applying this method are Sherritt Gordon Mines Limited at Fort Saskatchewan in Alberta, Canadian Electrolytic Zinc Limited at Valleyfield, Quebec, and Hudson Bay Mining and Smelting Company at Flin Flon, Manitoba.

### 1.1 Pressure Leaching

A typical zinc concentrate consists of about 50% zinc, 30% sulphur, 10% iron, 5% water, 2% lead and less than 1% copper and cadmium.

In the pressure leaching process the zinc concentrate is wet ground to particles of less than 325 mesh to make sure that all the concentrate reacts in the pressure leach reactor. The slurry in the autoclave is mixed with sulphuric acid, obtained as recycled electrolyte from the electrowinning unit. The autoclave is a cylindrical vessel, the exterior shell constructed of mild steel which is lead-lined and lined again with acid resistant bricks. The autoclave is subdivided into four sections each supplied with a titanium mixer and baffles to enhance mixing. The preheated slurry mixture enters the autoclave at about 343 K (70°C). Oxygen is pressured into the

autoclave to a partial pressure of 1.034 MPa (150 psi). The reactions in the autoclave are exothermic and take place at 428 K (150°C). Zinc sulphide and all other metal sulphides present react with oxygen and sulphuric acid to produce sulphates, elemental sulphur and water.

The sulphur from the autoclave is recovered by means of flotation. In the case of a pressure leaching plant integrated with the roast leach process, the process stream is combined with the conventional plant stream at the acid leaching stage. The combined process stream is thickened to remove precipitates, neutralized and purified before it is sent to the electrowinning unit to recover the zinc metal. A simplified flow diagram for the pressure leaching process is presented in Figure 1.

## 1.2 Advantages of the Pressure Leaching Process

The pressure leaching process has the potential of providing a means for significantly reducing sulphur dioxide emissions to the atmosphere and, hence, for reducing acid rain. This is possible because in the pressure leaching operation the solid metallic sulphide is transformed into the dissolved metallic sulphate and elemental sulphur without ever producing sulphur dioxide. This process is, therefore, a significant advancement as an environmental pollution control method.

There are several other advantages for using the pressure leaching process. These will now be summarized.

In the older, conventional process, the economic and environmental concerns dictate that the capacity and operation of the zinc plant must be matched with that of sulphuric acid plant. This constraint is eliminated in the new pressure leaching process since the elemental sulphur product can be stored and used when required. Further, in the conventional process a residue resistant to acid leaching, namely zinc ferrite ( $ZnFe_2O_4$ ), is produced. To recover zinc from this compound extra treatment is needed. Hot gases and dusty solids are produced in the roaster. These cause a hygienic problem. In pressure leaching all reactions take place in a slurry within the pressure leaching autoclave. This improves the plant hygiene. Nor is there a zinc residue from pressure leaching.

Finally, there is a possible economic saving. When Cominco introduced pressure leaching (Whiteside, 1979) it was estimated that there would be a 20 to 25 percent saving in capital investment. Additional savings were expected because of the reduced labour requirement.

Thus, the pressure leaching process has both economic as well as environmental benefits.

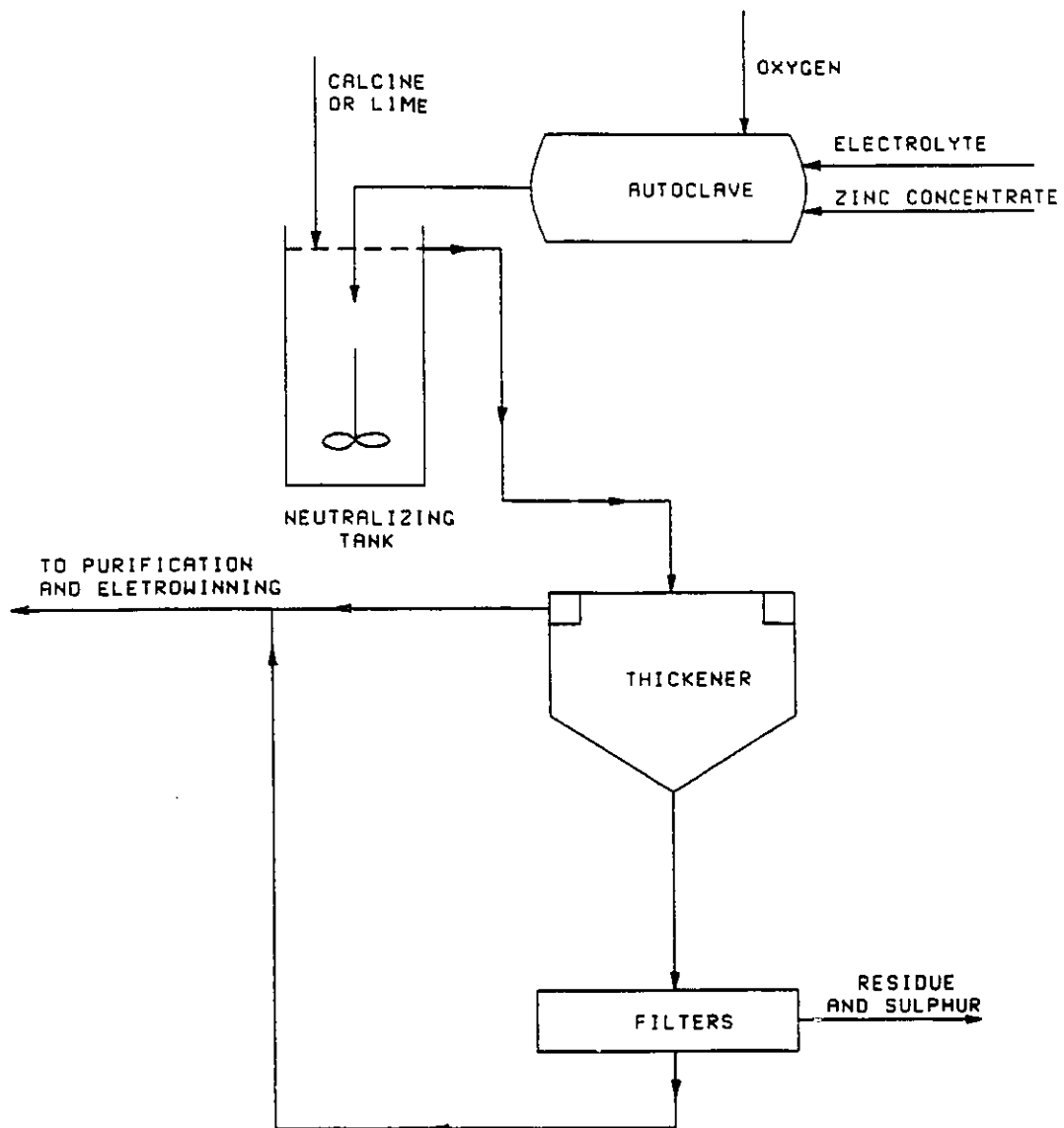
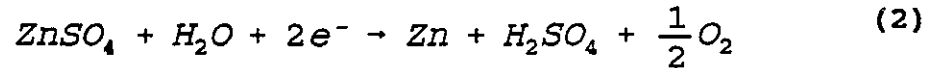


Figure 1. A Simplified Flow Diagram for a Pressure Leaching Plant.

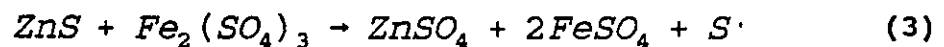
The electrowinning of zinc sulphate to recover zinc can be expressed by the overall equation:



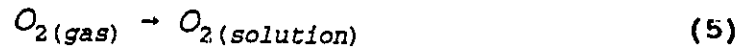
The overall recovery of zinc using this process is 97 to 98 percent. Losses occur during purification when substances other than zinc sulphate are separated.

### 1.2.1 Process Chemistry and Kinetics

The zinc pressure leach process is expressed by the overall reaction given by Equation 1. However, studies conducted for the process (Chalkley and Weir, 1983) indicate that the process is too slow to have any practical use without species that facilitate oxygen transfer. Acid soluble iron, found in the zinc concentrate is such a species. Iron is a catalyst for the reaction. Actually, therefore, the overall reaction is the sum of two reactions:

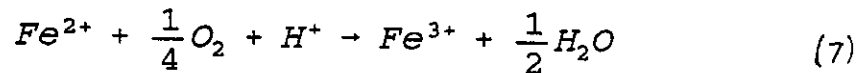


Recent work investigating the kinetics of the Sherrit Gordon zinc process (Dreisinger et al., 1990), has revealed that the kinetics are affected by three controlling steps. The controlling steps are expressed by respective rate equations which were empirically determined. The first is the oxygen mass transfer from the gas to the leach solution:



$$Rate = k_{g/l} ([O_2]_{(gas)} - [O_2]_{(solution)}) \quad (6)$$

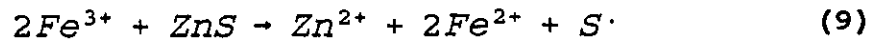
The rate of oxygen mass transfer was found to be a maximum at a certain critical agitation speed. The second step involved the homogeneous oxidation of ferrous ion to ferric ion by dissolved oxygen:



$$Rate = k_2 [Fe^{2+}] [O_2]_{solution} \quad (8)$$

It was observed that the rate of oxidation of ferrous ion is favoured by increase in the concentration of zinc sulphate, an increase in temperature between 393 and 428 K as well as the presence of copper sulphate in the leach solution. However, it was also found that an increase in the concentration of sulphuric acid and an increase in temperature above 425 K decreased the oxidation rate.

Finally, the third step of the leaching process involved ferric ion leaching of zinc sulphide:



$$Rate = k_3 [Fe^{3+}] A_{ZnS} \quad (10)$$

Equations (6), (8) and (10) must be solved in order to describe the operation of pressure leaching plants and for effective plant design. Equations (6) and (8) cannot be solved without knowing the concentration of oxygen in the solution. This amount is represented as  $[O_2]_{\text{solution}}$ . The maximum amount of oxygen in the solution corresponds to the equilibrium solubility of this gas under the operation conditions. Because the pressure leaching is a new process, oxygen solubility data for various aqueous sulphuric acid, zinc and iron sulphate solutions are not known but are required for design calculations. This project is the result of a CANMET contract to provide solubility data for zinc processes using the pressure leaching process. This project has been particularly challenging with regards to the design of experimental equipment for high temperatures, and pressures and extremely corrosive solutions.

### 1.3 Solubility of Oxygen in Sulphuric Acid Solutions

Very few workers have measured the solubility of oxygen in aqueous sulphuric acid solutions. Those who did, did not cover sufficient common ranges of concentration and temperature for direct comparison. The data available are thus, considered tentative only.

In the review of oxygen solubility data done by IUPAC (Battino, 1981), it was shown that by 1980 there were only six recorded sets of measurements for the solubility of oxygen in aqueous sulphuric acid solutions. Half of the measurements were carried out just after 1900. The rest were reported in 1965 and 1967. The data are too scattered for a direct comparison by interpolation or extrapolation. However, all the results indicate the following trends:

At a given temperature and partial pressure of oxygen, the solubility decreases with an increase in the sulphuric acid concentration. The solubility increases with the increase in the partial pressure of oxygen at a constant temperature and concentration.

Measurements made by Bruhn et al. (1965), at five temperatures between 323 and 523 K and for concentrations of 0.5, 1.0 and 1.5 mol/L sulphuric acid solutions, show a decrease in the solubility from 323 to 373 K. This is followed by an increase from 373 to 423, 473 and to 523 K. Thus, a minimum solubility was indicated at 373 K.

Kleva (1967) is the only person who measured the solubility of oxygen in aqueous sulphuric acid solutions containing salts. He measured the solubility at oxygen partial pressure of 0.25 and 1.0 MPa (2.5 and 10 atm) at six temperatures between 323 and 473 K. The concentration of the solutions was 0.0125 mol/L sulphuric acid and saturated with either nickel sulphide ( $\text{NiS}_2$ ), Copper sulphide ( $\text{Cu}_2\text{S}$ ) or Cobalt sulphide ( $\text{Co}_3\text{S}_2$ ). The actual sulphide concentrations were not given. The sulphuric acid-metal sulphide solutions decreased the oxygen solubility to less than 50 percent its solubility in water. The variation of oxygen solubility with temperature and partial pressure of oxygen followed the same trend as that for the plain sulphuric acid solutions.

#### 1.4 Densities of Aqueous Solutions

In chemical engineering, densities of solutions are used for material balances of processes where stream flows and concentrations are characterized by means of volume. The pressure leaching process is no exception.

Most of the tables of densities of aqueous sulphuric acid solutions (Söhnel and Noxtniný, 1985; Perry, 1984) are for binary systems only, and are limited to a maximum temperature of 373 K (100°C). Extrapolation of these values cannot give correct results for the temperature range and most of the compositions of solutions used in this work.

## 1.5 Scope of the Research

This research is aimed at determining the equilibrium solubility of oxygen in an aqueous sulphuric acid solution and four other solutions containing different amounts of the dissolved salts, hydrated zinc and ferric sulphate. The measurements of solubility were conducted for a range of temperatures and pressures. Measurements were carried out at 368, 398, 428 and 458 K and partial pressures of oxygen of 0.4053, 0.7093, and 1.013 MPa for the first three temperatures. Because of the high vapour pressure of the solutions at 458 K and the equipment limitations at pressures exceeding 2.068 MPa (300 psia), the three oxygen pressures chosen for the solubility determinations at that temperature were 0.2027, 0.4053 and 0.7093 MPa.

Solubilities were measured in solutions containing sulphuric acid, zinc and iron of the concentrations expressed as g/L for the three components, respectively, of (i) 5,0,0 (ii) 5,110,0 (iii) 5,110,1 (iv) 60,75,0 and (v) 60,75,10. For reference purposes, the solubility of oxygen was also measured in water at the temperatures and pressures specified above.

For the above five solutions, the densities were also determined at all the above conditions of temperature and pressure. The solutions and conditions were chosen to simulate those solutions and conditions used for pressure leaching of zinc sulphide ores.

## 1.6 Experimental Difficulties

Several experimental difficulties experienced in this research will be mentioned here. First, dilute sulphuric acid solutions can be handled safely, without excessive corrosion in stainless steel at low temperatures, but these same solutions become extremely corrosive at the higher temperatures, above 373 K (100°C). For this reason experimental equipment normally used for this purpose could not be used to measure density or oxygen solubility but instead needed to be completely redesigned to allow for the corrosiveness of the solutions. Next, because the solubility of oxygen in these solutions for the conditions chosen was generally extremely low, special modifications to the experimental procedure were required to allow for the measurement of very small volumes of gas in relatively big volumes of solution. Finally, when the solutions that were highly concentrated with salts were left to cool to room temperature, the salts blocked the tubes used to convey the saturated solutions to the desorption apparatus. The tubing could not be unblocked by washing, blowing and even heating. This problem occurred especially at the temperatures of 428 and 458 K and required the replacement of the blocked tubes.

## 2. THEORETICAL ASPECTS

### 2.1 Salt Effects

Studies concerning the effect of dissolved salts on the solubility of gases are well presented by Long and McDerit (1952) and Battino and Clever (1966) and also summarized by IUPAC (Battino, 1981). The magnitude of the effect of salts on the activity coefficient of a dissolved gas in aqueous solutions depends strongly on the properties of all solute species, which include the nonelectrolyte (or gas) and the salt. At a given temperature and pressure and when there is negligible chemical interaction between solute species, the logarithm of the dissolved gas activity coefficient can be represented as:

$$\log \gamma_i = k_s C_s + k_i C_i \quad (11)$$

In this expression  $k_s$  is the salt effect parameter,  $C_s$  is the electrolyte concentration,  $k_i$  is the solute-solute gas interaction parameter and  $C_i$  is the nonelectrolyte solute gas concentration.

It is considered that the dissolved gas activity is the same in the pure solvent as it is in a salt solution in that solvent as follows:

$$a_i = \gamma_i S_i = \gamma_i^{\circ} S_i^{\circ} \quad (12)$$

$$\gamma_i = \gamma_i^{\circ} \frac{S_i^{\circ}}{S_i} \quad (13)$$

In the above equations  $S_i$ , and  $S_i^{\circ}$  are the gas solubilities in the solution, and in the pure solvent, respectively. Also,  $\gamma_i$  and  $\gamma_i^{\circ}$  are their corresponding activity coefficients. Therefore, the following equation results:

$$\log \frac{\gamma_i}{\gamma_i^{\circ}} = \log \frac{S_i^{\circ}}{S_i} - k_s C_s + k_i (C_i - C_i^{\circ}) \quad (14)$$

If the nonelectrolyte solubilities are low, as they generally are for a gas, the term with  $k_i$  can be neglected, even if  $k_i$  is similar in magnitude to  $k_s$ . Thus:

$$\log \frac{\gamma_i}{\gamma_i^{\circ}} = \log \frac{S_i^{\circ}}{S_i} - k_s C_s \quad (15)$$

In some experiments the requirements set above are not always met. The experimental Setschenow salt effect parameter,  $k_{scs}$ , is, therefore, mostly used. This enables comparison of data obtained by different workers, especially when comparing the effect of a salt on a gas of low solubility with one of high solubility. The Setschenow salt effect parameter is given by:

$$k_{sca} = \frac{1}{C_2} \log\left(\frac{\alpha^0}{\alpha}\right) \quad (16)$$

In the above expression  $C_2$  is the electrolyte concentration in mol/L and  $\alpha^0/\alpha$  is the Bunsen coefficient ratio. The Bunsen coefficient is defined as:

$$\alpha = \frac{V_{(g)}}{V_{(l)}} \frac{273.15}{T} \quad (17)$$

In the above equation  $V_{(g)}$  is the volume of gas absorbed, and  $V_{(l)}$  is the volume of absorbing solvent at the temperature of measurement.

The salt that increases the activity coefficient of the dissolved gas is said to salt out the gas and the salt that decreases the activity coefficient of the dissolved gas is said to salt in the gas. Salting out means decreasing the solubility of the gas, whereas salting in implies increasing its solubility.

The solubility of gases in water is usually decreased by the addition of other solutes, particularly electrolytes. The extent of this salting out varies considerably with different salts, gases, solvents and temperature.

## 2.2 Vapour Pressure of Aqueous Solutions

The vapour pressure of a liquid is a function of temperature and increases rapidly with temperature. The presence of a non-volatile solute lowers the vapour pressure of the solution by an amount proportional to the mole fraction of the solute. Non-volatile solutes are generally solids which yield a negligible contribution to the vapour pressure above the solution. The lowering of vapour pressure by a non-volatile solute is directly implied by Raoult's law. For ideal solutions, Raoult's law is usually expressed in terms of the solvent mole fraction as follows:

$$p = x_A P^\circ \quad (18)$$

For the solute mole fraction:

$$p = (1 - x_B) P^\circ \quad (19)$$

### 2.2.1 Non Ideal Solutions

The activity,  $a$ , of a component in a particular solution is considered to be the ratio of its fugacity in the solution to that in some arbitrarily chosen "standard state" expressed

as follows:

$$a = \frac{f}{f^{\circ}} \quad (20)$$

In an ideal solution (Shinoda, 1978) the partial pressure of each component is proportional to its mole fraction. Therefore the activity of each component is equal to the mole fraction:

$$a = \frac{f}{f^{\circ}} = \frac{p}{P^{\circ}} = x \quad (21)$$

The activity of a component is not equal to its mole fraction in a non-ideal solution. It becomes convenient to use the activity coefficient defined as:

$$\gamma_A = \frac{a_A}{x_A} \quad (22)$$

$$\gamma_B = \frac{a_B}{x_B} \quad (23)$$

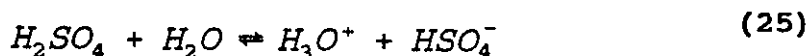
It has been shown that the Raoult's law can be modified as follows (Levine, 1978):

$$p = (1 - \gamma_B x_B) P^{\circ} \quad (24)$$

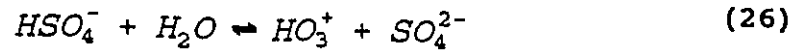
The activity coefficient,  $\gamma_g$ , represents the degree of deviation of the component's behaviour from the ideal. It can be viewed as a correction of the mole fraction for non-ideality.

### 2.2.2 Solutions of Electrolytes

An electrolyte is a substance that produces ions in solution. This is indicated by the solution's ability to conduct electricity. In a given solvent, an electrolyte is classified as weak or strong. At moderate concentrations, a weak electrolyte is a poor conductor of electricity whereas, a strong electrolyte is a good conductor of electricity. Electrolytes are also categorized as true or potential electrolytes. A true electrolyte consists of ions in the pure state. Most salts are true electrolytes. Potential electrolytes consist of uncharged molecules in the pure state, but when they are dissolved in a solvent they react chemically with the solvent to some extent to yield ions. For example, sulphuric acid reacts with water according to:



In a dilute solution, a further reaction occurs:



In the pure liquid state, a true electrolyte is a good conductor of electricity. In contrast, a potential electrolyte is a poor conductor of electricity in the pure state.

In electrolyte solutions there is always both dissociation and association of ions taking place. The extent of each is difficult to determine. Because of the strong, long range repulsive and attractive forces between ions in electrolyte solution, the use of activity coefficient in dealing with electrolyte solutions is essential. It is essential for concentrated solutions and even for quite dilute solutions.

### 2.3 Vapour Pressure of a Volatile Solute

For dilute solutions, the vapour pressure of a volatile substance in a solution is linearly related to the mole fraction. This relation is explained by Henry's law, which states that the partial pressure of a volatile solute above the solution is proportional to the mole fraction of that solute in the solution:

$$p_B = K_H x_B \quad (27)$$

Henry's law constant depends on the properties of the solute and the solvent. The physical basis of Henry's law is that for dilute solutions, every solute molecule is completely surrounded by solvent molecules. Provided this condition prevails, the vapour pressure of the volatile solute will be proportional to its mole fraction. If the solvent and gas does not react chemically, the solubility of gases in liquids is usually small and the solution can be considered dilute. Henry's law has a special significance for the solubility of gases in liquids. It can be used for converting solubility data from the experimental pressure to a partial pressure of one atmosphere, for example, provided the mole fraction of the gas is small. It is recommended that for a solubility of gas of less than 0.01 mole fraction Henry's law can be used (Battino, 1981).

#### 2.4 Effects of Pressure on The Density of a Solution

The dependence of volume on pressure is given by:

$$V = V_0 [1 - \kappa (p_v - 1)] \quad (28)$$

In the above expression  $V_0$  is the volume at 273 K for a pressure of 101.3 kPa,  $p_v$  is the pressure in atmospheres, and  $\kappa$  is the coefficient of compressibility. This value is constant for a particular liquid over fairly wide ranges of pressures. Values of  $\kappa$  for liquids and solids are extremely small, being of the order of  $10^{-6}$  to  $10^{-5} \text{ atm}^{-1}$  (Castellan,

1983). If we take  $\kappa = 10^{-5} \text{ atm}^{-1}$ , then for a pressure of eleven atmospheres the volume of liquid is:

$$V = V_0[1 - 10^{-5} \times 10] \quad (29)$$

The decrease in volume in going from one atmosphere to eleven atmospheres is only 0.01 %. Because moderate pressure changes produce very tiny changes in the volume of liquids, like solids, they are considered to be incompressible ( $\kappa = 0$ ).

Therefore, the effect of pressure on the density of liquids can be neglected for all except very high pressures. However, a pressure higher than the vapour pressure of the liquid must be applied on the solution to prevent the liquid from boiling or excessive vaporization during the measurement of density.

### 3. METHODOLOGY

In this chapter the experimental apparatus and procedures are explained. Methods used in the measurement of the densities of solutions and the solubilities of oxygen in these solutions are described. There is also a section dealing with calculation methods.

#### 3.1 Experimental Equipment Development

Severe corrosiveness of the solutions used in this work at higher temperatures, made it necessary to design the equipment to withstand the severe corrosiveness involved. A two-step absorption-desorption equipment was designed for measuring oxygen solubilities and a pyrex glass dilatometer apparatus for measuring the densities of the solutions.

##### 3.1.1 Solubility Measurement

The solubilities of oxygen were measured in a two-step, absorption-desorption apparatus. A similar arrangement was used by Choudhary et al. (1982), for the measurement of solubilities of gases at high pressure. However, while they used a different apparatus for the desorption part, they did describe their high pressure and high temperature autoclave. Because of the severe corrosiveness of the solutions

encountered in this work, special attention was given to the design of the absorption vessel. The desorption apparatus used in this work was a spiral tube solubility apparatus. It was first proposed by Morrison and Billet (1948), and modified by Hayduk and Cheng (1970) and others. In this work, the spiral tube apparatus was used in a different way. While the previous workers used it for absorbing gases to saturate solvents, this time it was used for desorbing oxygen from the saturated solutions. Also, instead of using a syringe-pump to supply solution to the apparatus, the pressure in the high pressure absorption vessel was used as a driving force to cause the solution to flow to the desorption apparatus. The flow was controlled by means of a needle valve.

#### 3.1.1.1 Absorption Vessel

The high pressure absorption apparatus consisted of a stainless steel (SS 316) pressure vessel with a solvent capacity of  $6 \times 10^{-4} \text{ m}^3$  (600 mL). The vessel was equipped with a pyrex glass insert or liner to prevent direct contact and hence corrosion of the stainless steel by sulphuric acid at high temperatures. A glass vessel was also easier to clean than a stainless steel one. It therefore reduced contamination of the solutions. The vessel was provided with a magnetic stirring system. The magnetic stirrer bar used was a conventional one consisting of an iron bar coated with

teflon to prevent corrosion. The magnetic stirrer inside the pyrex glass vessel could be operated even though the pressure vessel was immersed in an insulated oil bath. The vessel was sealed at the top by using a teflon gasket and six stainless steel tightening bolts.

A  $3.175 \times 10^{-3}$  m (1/8-inch) stainless steel (SS 316) tube was immersed in the aqueous sulphuric acid-salt solution inside the pyrex vessel. The tube inside the vessel was covered on the outside with a teflon sleeve. The sleeve protected the tube from possible erosion-corrosion attack, which is a corrosion attack accelerated by the flow or impingement and in which the protective products of corrosion are swept away by the flow conditions. This tube was used in discharging the solution after equilibrium was reached and conveying it to the desorption apparatus. The hottest part of the tube, (the one that was within the oil bath), was observed to become corroded by the hot sulphuric acid- metallic salt solution at 428 K and 458 K, that contained 60 g/L sulphuric acid and 75 g/L zinc ( $Zn^{2+}$ ) but that contained no iron salt. Not only was the tube corroded but also some gas (probably hydrogen) was evolved when the hot solution was passed through it. This gas interfered with the quantitative determination of oxygen.

The tube was therefore changed to a titanium one. Titanium is the material that is used in the pressure leaching process for equipment immersed in a sulphuric acid solution,

such as agitators or baffles. It was found, however, that the solution containing 60 g/L acid without iron salt still corroded the titanium tube at the temperatures mentioned above. Advice was received from Dr. E. Peters, Professor of Metallurgical Process Engineering at University of British Columbia, concerning this problem. He indicated that ferric ions (or other oxidized ions such as copper) must be present in hot sulphuric acid to passivate the titanium. A level of 2 g/L of ferric iron (Uhling, 1971) was recommended for this purpose. For that reason this level of ferric ion was used for the solution mentioned above which was originally specified to contain no iron for the temperatures of 428 and 458 K. In fact, in the pressure leaching process, the leaching solutions contain sufficient ferric or cupric ion (Othmer, 19824a), to inhibit the corrosion of the titanium. Indeed, it was then possible to determine the oxygen solubility in this solution at the two temperatures without interference.

The high temperature oil bath was a TMV 45DD visibility bath obtained from Neslab Instruments. The temperature controller for the insulated constant temperature bath maintained a temperature to within 0.1 K. Of special note is that for the sake of economy, safety and convenience the bath oil was an edible peanut oil. The oil could be used continuously at high temperatures for up to one month before decomposition occurred. After this time period the peanut oil

became somewhat viscous and was replaced with fresh oil. For safety reasons the high pressure and temperature absorption part of the equipment was mounted in a fume hood.

Stainless steel tubing was used to connect the absorption apparatus to a vacuum pump through a vapour trap, to a hand pump, a pressure transducer and an oxygen supply. The vacuum pump was used for degassing the solution in the absorption vessel. It was capable of giving an almost complete vacuum. The vapour from the absorption vessel passed through an ice-cooled trap. The function of the trap was to reduce the amount of vapour going into the vacuum oil inside the pump. This in turn reduced the deterioration of the vacuum oil. The hand pump was used for fine adjustment of pressure during equilibration. The hand pump had a vernier scale that could give an accurate gas volume to  $1 \times 10^{-8} \text{ m}^3$  (0.01 mL) and it had a total gas capacity of  $1 \times 10^{-4} \text{ m}^3$  (100 mL). A high precision transducer system had a digital readout readable to 68 Pa (0.01 psi). The transducer could work in a pressure range of 0 to 2.068 MPa (0 to 300 psia). A schematic flow diagram of the High Pressure Solubility Equipment is shown in Figure 2.

The two-stage absorption-desorption equipment was used because a simpler single-stage volumetric method could not give reasonably reliable measurements. A considerable period of time was spent in attempting to develop an accurate but simpler, single-stage volumetric method for measuring oxygen

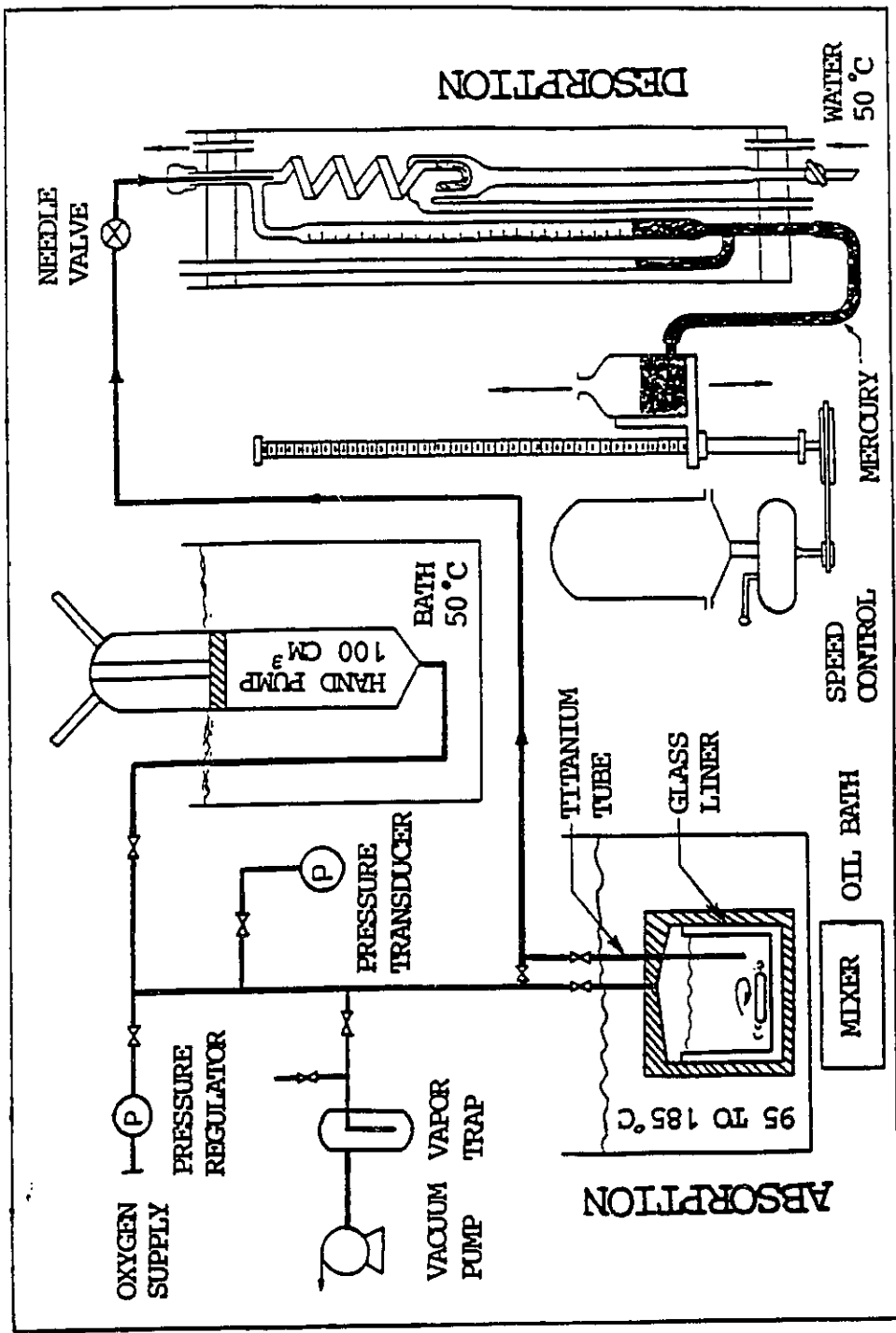


Figure 2. High Pressure Solubility Equipment

solubilities in the acid solutions at high pressures. This was attempted by adding a measurable volume of oxygen at constant pressure and temperature to an absorption cell from the variable-volume piston device. This necessarily would have required an accurate determination of pressure and also for residual oxygen volume. For this purpose, an accurate transducer and readout instrument ( to 0.01 psi ) was used as well as a piston pump calibrated to  $1 \times 10^{-8} \text{ m}^3$  (0.01 mL). Nonetheless, the actual volume of oxygen dissolving in the various acid-salt solutions was simply too small (5 to 10 mL per 1000 mL of solution) to be accurately determined. Often there was some small amount of leakage at the gasket of the absorption vessel. In addition, because of some thermal effects in the absorption vessel, a prolonged period of time was required to reach thermal equilibrium and subsequently saturation of the solution. The time that would have been required to obtain one result at one pressure was about 12 hours. Therefore, there were two reasons why the simple one-step absorption method for oxygen was impractical. The first was that the time required for each experiment was excessive and the next was that the determination of the volume of gas absorbed was not sufficiently accurate. For these reasons the two-stage process was adopted for these experiments.

The two-stage process had definite advantages over the single-stage one. The small amount of gas that dissolved at high pressure was expanded as it was released at atmospheric

pressure, giving a reasonably measurable amount of gas for a smaller quantity of solution. It was therefore, possible to determine the solubility of oxygen in one solution at one temperature for three different pressures using one charge of about  $5 \times 10^{-4} \text{ m}^3$  (500 mL) of solution. Thus, a relatively small vessel in which equilibrium could be reached faster could be used. Also, the apparatus could be used even when there was a small amount of leakage in the absorption vessel. In addition, the two-stage procedure gave oxygen that was only physically dissolved in the solution. Thus, it was not necessary to check for the possibility of reaction between the gas and the acid solution. Another advantage was that the arrangement did not require the immersion of a temperature probe inside the absorption vessel itself; a temperature probe could have been corroded and hence, could have lead to contamination of the solutions. The relatively small high pressure absorption vessel was totally immersed in the constant temperature bath.

### 3.1.1.2 Desorption Apparatus

The quantity of dissolved oxygen contained in the acid solution, saturated at higher pressures and temperatures, was measured in a glass desorption apparatus. It consisted essentially of a spiral glass tube mounted inside a transparent plastic jacket. This apparatus was operated at atmospheric pressure and a temperature of 323 K (50°C). The temperature of 323 K was maintained by circulating hot water through the jacket surrounding the apparatus. The operating temperature of 323 K was chosen because this temperature was near the temperature for which the oxygen solubility in water was a minimum (about 100°C) and for which the evaporation rate of water was relatively low.

The glass apparatus consisted of a spiral coil through which the solvent, saturated with oxygen, flowed as a thin film, releasing the oxygen. The coil was connected at the top to a burette initially filled with mercury. At the bottom it was connected to a small U-tube manometer through which the solvent flowed. The small U-tube manometer acted as a seal, confining the gas in the spiral coil between it and the mercury-filled burette. The manometer also served as a very sensitive pressure indicator for comparing the internal pressure with the atmospheric pressure. The confined volume could be increased as the oxygen was released, by lowering the level of mercury in the burette. Because it was difficult to

steadily lower the mercury level, a motorized screw device, driven by a variable-speed motor, was used for that purpose. The mercury in the gas burette could be lowered at a rate just sufficient to keep the pressure in the apparatus constant as required. The solution from the absorption vessel, equilibrated at high pressure, was supplied to the desorption apparatus through a needle valve. The function of the needle valve was to control the flow rate of the solution into the desorption apparatus at constant rate and to reduce the pressure from the value in the absorption vessel to the one in the desorption apparatus.

### 3.1.2 Densities of Solutions

The densities of the solutions were measured at temperatures ranging from 298 to 458 K (25 to 185°C). At temperatures of 298 and 323 K a digital precision, vibrating-reed density meter was used. To avoid corroding this rather expensive equipment at higher temperatures, and the fact that its operation was limited to 423 K (150°C), a set of dilatometers were used, for the measurement of densities at higher temperatures. The dilatometers were used to measure the dilation of the solutions as the temperature was increased. The dilatometers were made of 0.008 m (8-mm) pyrex glass capillary tubes of uniform cross-sectional area. One end of each tube was sealed by glass blowing methods. The

open end was then fitted to the (1/8-in) stainless steel tubing system for pressurising, through a (3/8 to 1/8-in) reducing union. Four such dilatometers were constructed. In the design and construction of the dilatometers it was found that the pyrex glass was very brittle and slippery. It broke easily when connected with the metallic fittings and when the system was pressurized or when the nuts were tightened. When the tubes were not firmly tightened on the other hand, they slipped out of the fittings on pressurizing.

The problem of slipping of the dilatometer tubes was solved by slightly expanding the open ends of the capillary tubes. Tubes of slightly smaller size were intentionally chosen for this purpose. The expansions were made in such a way that the top of the tube just fitted inside the fittings. Breakage was minimized by using specially made teflon ferrules instead of the stainless steel ones, to provide the necessary seal. Because of expansion of the ends of the tubes, it was possible to get a firm connection by just tightening the fittings lightly. Also, the fittings were fixed to the pressurizing system in such a way that they did not contact the hot oil. The reason for this was to reduce the thermal expansion and hence, loosening of the fittings. Eventually, the capillary tubes could be pressurized (to 12 atm) without breaking or slipping out of the fittings. A flow diagram of the Dilatometer Density Apparatus is presented in Figure 3.

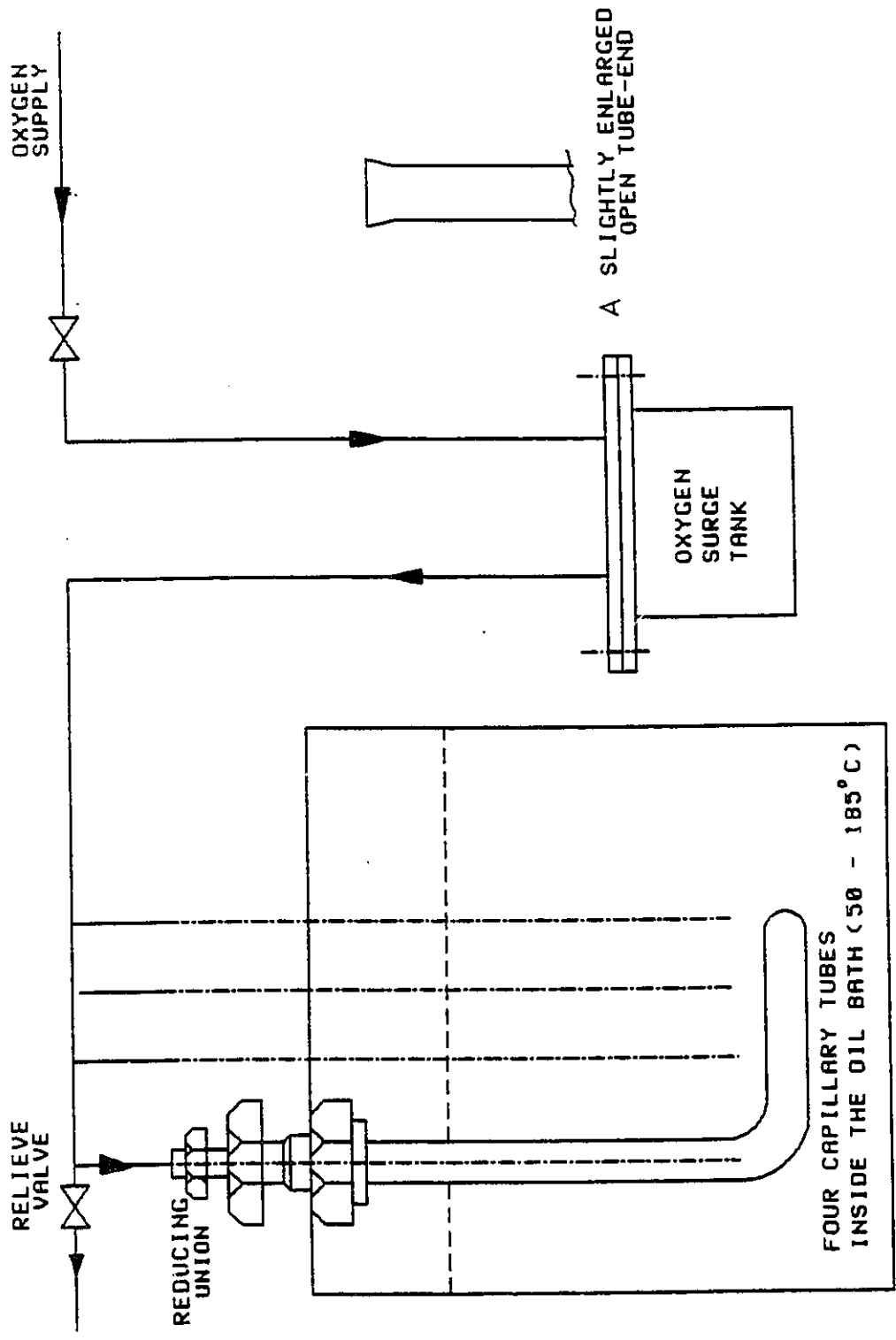


Figure 3. Dilatometer Tubes Density Apparatus

To obtain sufficiently measurable dilations of the solutions, it was important to make the capillary tubes as long as possible. Because of the limited depth of the constant temperature bath, to about 0.25 m, the capillary tubes were bent to form a 90° angle. In this way, it was then possible to construct the capillary tubes with exposed (transparent) lengths of 0.531, 0.540, 0.547 and 0.571 m. The same high temperature oil bath used for oxygen solubility experiments was used to heat the solutions inside the dilatometers.

### 3.2 Experimental Procedure

The aqueous sulphuric acid-metallic salt solutions used in this work were those specified in the Section 1.5. For all the solutions, the experimental procedures used for determining both the densities and oxygen solubilities are explained in this section.

#### 3.2.1 Preparation of Solutions

The experimental solutions were prepared from a hydrated ferric sulphate powder of 73.2% ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3$ ), obtained from J.T. Baker Chemical Co., a 96.0% sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and 99.5% hydrated zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) from BDH Inc. All these chemicals were of analytical grade. The

amounts of sulphuric acid needed to give the desired concentrations were measured accurately by using a burette readable to  $5 \times 10^{-8} \text{ m}^3$  (0.05 mL). The acid solution was prepared first, titrating the concentrated acid into distilled water. The amounts of zinc sulphate and iron sulphate were weighed by means of a Metler analytical balance in the required amounts. The analytical balance gave accurate measurements to  $1 \times 10^{-8} \text{ kg}$  (0.01 mg). Appropriate amounts of these chemicals were dissolved in the dilute acid. Appropriate amounts were then diluted to yield the required concentrations in volumetric flasks. Sample calculations for determining the correct amounts of the chemicals for the preparation of the solutions are given in Appendix B. As a means of checking for gross errors in the preparation of the solutions, densities of newly prepared solutions were measured and compared with the densities at 298 K of previously prepared solutions of the same composition.

### 3.2.2 Determination of Oxygen Solubility

A two-step method for determining the high pressure and high temperature solubilities was used. First, oxygen was absorbed at constant pressure and temperature in the high pressure absorber (vessel), at a pressure yielding an oxygen partial pressure of 1.013 MPa (10 atm) in the degassed acid-salts solution. When equilibrium was achieved, a stream of

saturated solution was directed through a needle valve to the glass desorption apparatus. The desorption apparatus was operated at atmospheric pressure and at a temperature of 323 K (50°C).

The sealed high pressure absorption vessel was charged with a sulphuric acid-metallic salt solution, through an inlet valve at the top by using the gravitational force. This procedure eliminated the need for frequent opening of the vessel, a practice that was observed to cause gas leakage at the gasket. The closed vessel was then immersed in the constant temperature oil bath and the solution was degassed.

Degassing was accomplished by applying a vacuum using the vacuum pump. This method was used for experiments carried out at 368 K (95°C) and when the solutions were heating up for experiments at higher temperatures. A vacuum of at least 89.6 kPa (13 psi) was maintained for 10 to 15 minutes. This pressure was the minimum observed to cause boiling of the solutions at room temperature. For high temperatures, the acid solution was degassed by intermittently purging some of the steam from the heated absorption vessel to the ice-cooled vapour trap before the solubility experiments were started. During the degassing procedure, the solution was agitated using the magnetic stirrer. The purpose of stirring was to continuously expose new liquid surfaces for effective degassing. The volume of solution evaporated (mainly water) in the process of degassing amounted to  $3 \times 10^{-6}$  to  $8 \times 10^{-6}$  m<sup>3</sup>

(3 to 8 mL). Thus, the small increase in acid and metal salt concentration as a result of degassing was considered to have a negligible effect on the oxygen solubility.

After degassing, the absorption vessel was pressurized with oxygen to a pressure equivalent to an oxygen partial pressure of 1.013 MPa (10 atm) and left to attain the desired temperature for at least four hours. During this period the solution was considered to have attained its equilibrium vapour pressure at the given temperature. A final adjustment in pressure was then made, and the equilibration continued over night. The total pressure of equilibration was the sum of the oxygen partial pressure and the estimated vapour pressure of the solution. The equilibration process involved continuous agitation of the solution in order to mix the oxygen and the solution. Without mixing the absorption of oxygen would have depended entirely on the process of diffusion which could have been practically too slow. It was observed that without agitation, solutions left overnight released essentially no gas when they were passed through the desorption apparatus the next day.

It was found that equilibrium conditions were easier to achieve in the high pressure absorber by initially starting at the highest partial pressure of oxygen (1.013 MPa), and subsequently reducing the oxygen pressure to 0.7093 MPa and then to 0.4053 MPa in turn. Also it was found that a shorter time was required to achieve saturation from an initially

supersaturated condition than that required to equilibrate an unsaturated solution. Thus, solubilities at the three pressures were measured with one charge of solution to the high pressure absorption vessel and starting with an initial oxygen pressure of 1.013 MPa.

The next morning the second step of the solubility determination, the desorption of the oxygen-saturated solution, was carried out. Prior to the desorption process, the desorption apparatus was flushed with pure oxygen. Next, the agitator in the absorption vessel was stopped to prevent further absorption during the desorption procedure. Then, about  $1 \times 10^{-4} \text{ m}^3$  (100 mL) of the saturated solution was slowly transferred to the desorption apparatus while maintaining a constant pressure in the high pressure vessel. To maintain this pressure and to avoid desorption of the solution inside the absorption vessel it was necessary to operate at a slightly higher pressure than the equilibrium one, during desorption. In most cases a pressure of 6.9 kPa (1 psi) higher was used. The solution was allowed to flow through the desorption apparatus for at least 15 minutes, before any measurement was taken. This time was required to get a steady flow of the solution in the desorption apparatus. It was found that a relatively low solution flow rate of about  $2.78 \times 10^{-8} \text{ m}^3/\text{s}$  (100 mL/h) was required in order to get complete desorption of the oxygen from the solutions. The dissolved oxygen which was released as the pressure was reduced was

collected in the gas burette over the mercury. As the pressure gradually rose in the gas-collecting system, the level of mercury in the burette was lowered by using the screw device. When steady flow conditions in the desorption apparatus were attained, the quantity of oxygen released at 323 K and atmospheric pressure was accurately determined by reading its volume directly from the gas burette. The corresponding volume of the solution from which the oxygen was released was measured in a separate burette at 298 K. The use of a separate burette for the liquid made it possible to use the same desorption apparatus for all solutions. Other workers (Hayduk et al., 1988; Hayduk and Pahlevanzaleh, 1987) had to use different sizes of burettes for this type of apparatus depending on the solubility of different gases. The use of the same apparatus helped in reducing the level of systematic errors.

Several pairs of readings of gas and solvent volumes (at least ten) were taken at suitable time intervals. Also, recorded was the atmospheric pressure at the beginning and the end of each desorption experiment. When a sufficient amount of data was collected, the flow of solution into the desorption apparatus was stopped. Next, the oxygen pressure was reduced to an oxygen partial pressure of 0.7093 MPa. An equilibration period with stirrer in operation of 2 to 3 hours was required before a second solubility determination was made at this lower pressure. This procedure was repeated again at

an oxygen partial pressure of 0.4053 MPa. The pressure vessel was then removed from the oil bath and the remaining solution was sucked out through the inlet valve by applying a vacuum. The vessel was cleaned, rinsed and recharged for the next solubility determination.

### 3.2.3 Density Measurements

The Anton Paar densitometer was used for the measurements of solvent densities. This densitometer consisted of two parts. One was the sensing unit DMA 602, which contained a U-shaped sample tube connected to a measuring oscillator. The other component was the DMA 60 which was a frequency counter and a digital display component. The high-precision vibrating reed density meter was calibrated by using distilled water and ethylene glycol. Both liquids have known densities in the range of temperature used in this work. Usually distilled water and air are used for this purpose. There were two reasons for choosing ethylene glycol instead of air as a calibrating fluid. First, it gave a density calibration near the expected range of the densities of the solutions, and second, it was less volatile than other liquids that were available at that time. The densitometer was then used to measure densities of the experimental solutions at 298 and 323 K. On each occasion, a sample was injected into the density meter by using a plastic syringe. Then, it was left to attain

the desired temperature. The desired temperature was reached when the vibrating frequency reading on the densitometer remained constant with time. The desired temperature in the densitometer was maintained by circulating water at constant temperature. Several readings of the vibrating frequency were taken for each solution at each temperature. The average for each was found and used in the calculation of the density of each solution.

At 368, 398, 428 and 458 K, the densities of the solutions were measured by using the dilatometers. The total exposed length of each capillary tube was measured by using a measuring rule. The solutions were charged into the capillary tubes using a long syringe. Air bubbles in the solution inside the tubes were removed by using a thin, flexible and long copper wire. In order to get measurable magnitudes of dilations, a minimum solution length of about 0.35 m was required. Then, the tubes were connected to a pressurizing system. An oxygen surge tank was connected to the system to stabilize the pressure by increasing the total volume of the gas in the system. Before heating, the whole system was pressurized to a total pressure above the vapour pressure of water at the desired temperature. This was done to prevent boiling of the solutions. The bath temperature was then raised to 323 K (50 °C). At this temperature the initial length of the solution inside the capillary tube was measured and recorded. The lengths were accurately measured by using

a cathetometer readable to 0.00001 m (0.01 mm). To increase the visibility inside the oil bath, a light bulb was put in the other side of the bath, opposite to the side where the cathetometer was. The method employed was to measure the difference in height from the bottom of the stainless steel fitting and the top of the column of the solution in the capillary tube. This difference was then subtracted from the total length of the tube measured at room temperature to obtain the actual length of the solution. Subsequent lengths were taken at 368, 398, 428 and 458 K. These lengths were afterwards used to calculate the densities of the respective solutions by using mass balances. As a check on the method, the dilatometers were calibrated using distilled water. The calibration gave small correction factors which accounted for the minor effects such as the evaporation of solutions and expansion of the tubes. The dilation of the solutions was clearly observable in every case being at least 0.7 cm.

### 3.3 Methods of Calculation

As explained in sections 3.1 and 3.2, the solutions saturated with oxygen at high temperatures and pressures were treated in the desorption apparatus for the recovery of oxygen released at 323 K (50°C). It can be assumed that equilibrium conditions existed at that temperature and the solutions exerted the equilibrium vapour pressures. Similarly, the

vapour pressures in the absorption vessel were considered to be the saturation vapour pressures at the high pressure operating conditions after equilibration. The vapour pressures were estimated by using the modified Raoult's law, Equation (24). In this equation the water-sulphuric acid vapour pressure corresponding to the acid concentration of the given solution was used as  $p^{\circ}$ .

Sulphuric acid solutions have known vapour pressures at certain concentrations (Perry, 1984) and these were interpolated to get the vapour pressures at the desired acid concentrations. Sample calculations are shown in Appendix B. The vapour pressures of solutions are presented in Chapter 4.

A computer program in Basic was employed to calculate the solubility of oxygen both in mole fraction and in grams per litre (g/L). Also calculated for all the pressures were the Henry's constants as well as the oxygen solubilities corresponding to an oxygen partial pressure of 0.1013 MPa. Then it was possible to calculate an average Henry's law constant and average oxygen solubility corresponding to an oxygen partial pressure of 101.3 kPa (1 atm) for each solution, and at each pressure and each temperature.

The solubilities were obtained by using a least squares relation between the volumes of oxygen released and the residual solvent volumes. The volume of oxygen obtained in this way included the volume or partial pressure of water vapour at the conditions of desorption (323 K). The dissolved

salts are non-volatile and the dissolved sulphuric acid is also essentially non-volatile. The actual number of moles of oxygen was obtained by substituting the partial pressure of oxygen and the total volume of gas in the ideal gas law:

$$PV_{(g)} = nRT \quad (30)$$

The oxygen partial pressure was the difference between atmospheric pressure and the vapour pressure of a solution at 323 K:

$$P_{O_2} = P_{atm} - VP \quad (31)$$

In this equation VP is the vapour pressure of the solution.

Using a basis of the number of moles dissolved in 0.001 m<sup>3</sup> (1 L) of solution, the solubility in gram per litre was obtained by multiplying the number of moles by the molecular weight of oxygen:

$$C_g = n_L M_{O_2} \quad (32)$$

The same basis of solution was used to calculate the mole fraction solubility of oxygen in each solution. The expression for mole fraction is:

$$x = \frac{n_{O_2}}{(n_{C_2} + n_{H_2O} + n_{H_2SO_4} + n_{Zn^{2+}} + n_{Fe^{3+}})} \quad (33)$$

Henry's constant was calculated by rearranging the Henry's law expression as follows:

$$K_H = \frac{P_{O_2}}{X} \quad (34)$$

In this expression  $P_{O_2}$  is the oxygen partial pressure at the particular conditions of absorption.

The Setschenow salt effect parameter was evaluated using Equation (16) and the Bunsen coefficient by using Equation (17). In calculating the Setschenow salt effect parameter the concentration of electrolyte included all the salts and the sulphuric acid present in the solution.

The densities were calculated in two stages. The first stage involved the calculations based on the readings obtained with the density meter. In this case the readings of vibrating frequency were related to the density as follows:

$$\rho_E - \rho_W = K(\tau_E^2 - \tau_W^2) \quad (35)$$

The values of the calibration constants at 298 and 323 K were found by utilizing the liquids, distilled water and ethylene glycol, with known densities. Using the calibration constant and the readings of vibrating frequency obtained from the density meter for each solution, the densities of all the solutions were determined.

The second stage involved the density calculations based on the dilations of solutions with increased temperatures obtained by using the dilatometers. For this purpose the principles of mass balances were applied. If the loss of water by evaporation is neglected, the mass of the solution is

supposed to be the same at all temperatures:

$$mass_{at\ 50^{\circ}C} = mass_{at\ T} = constant \quad (36)$$

The mass can also be expressed in terms of the density of the solutions, the cross-sectional area of the capillary tube and the length of the solution inside the tube:

$$mass_{at\ 50^{\circ}C} = \rho_{50^{\circ}C} A_{50^{\circ}C} L_{e50^{\circ}C} = \rho_T A_T L_{eT} \quad (37)$$

The capillary tubes used in these experiments were of uniform cross-sectional area. Therefore, Equation (37) becomes, in general:

$$\rho_1 L_{e1} = \rho_T L_{eT} \quad (38)$$

By using the precise densities measured at 323 K and the lengths of the solutions measured at the higher temperatures, it was possible to calculate the densities at all conditions. To compensate for possible liquid evaporation of solutions, expansion of the tubes and the systematic errors in the method of measurement, the tubes were calibrated using distilled water. Correction factors were calculated from the ratio of the actual density of water available in literature (Keenan, 1969) and the calculated values:

$$r = \frac{\rho_{act}}{\rho_{me}} = \frac{mass}{AL_{eact}} * \frac{AL_{eme}}{mass} \quad (39)$$

The correction factor for each tube was used to calculate the

actual density of each solution at each temperature by correcting the measured length of the solution. This was possible by rearranging Equation (39):

$$L_{eact} = \frac{1}{I} L_{eme} \quad (40)$$

Sample calculations are presented in Appendix B and the Basic computer program in Appendix C.

#### 4. PROPERTIES OF MATERIALS

The oxygen used in this work was obtained from Air Products and Chemicals, Inc. It had a specified purity of 99.9%. Oxygen is almost an ideal gas in the range of temperature and pressure used in this work and corrections for non-ideality are not necessary. At 298 K and 101.3 kPa, the compressibility of oxygen is 0.9994 and increases to 1.002 at 500 K (Perry, 1984). These values lead to corrections for non-ideality of 0.06%, and 0.2%, at 298, and 500 K, respectively. The corrections are negligibly small compared to the general accuracy of this work estimated to be in the range of from 2.0% to 4.0%. The use of the ideal gas law without correction for the non-ideality of oxygen at low and moderate pressure was also recommended by Battino (1981).

The ethylene glycol was purchased from BDH Chemicals and had a minimum purity of 99.5%. The density of this chemical at 298 K and 323 K was taken from literature (Gallant, 1968; Wong and Hayduk, 1990).

The leach solutions, as specified in section 1.5, were prepared from concentrated sulphuric acid, hydrated zinc sulphate and iron sulphate as described in section 3.2. The vapour pressures of the solutions at the experimental temperatures were estimated by using Figure 9 and Equation (24) in Appendix B. The results are presented in Table 1. The densities of these solutions were measured as part of this work and are presented in the Results section.

**Table 1. Vapour Pressure of Solutions in kPa as Estimated Using a Modified Raoult's Law.**

Temperature, K	323	368	398	428	458
Solutions					
Water	12.3	84.5	230.0	540.0	1118.0
‡5/0/0	12.3	84.3	229.3	538.0	1112.9
5/110/0	12.3	82.3	224.0	525.5	1086.9
5/110/1	12.3	82.3	223.9	525.4	1086.8
60/75/0	11.8	80.5	218.7	509.3	1042.7
60/75/10	11.8	80.3	218.4	508.5	1040.9

‡ H<sub>2</sub>SO<sub>4</sub> in g/L / Zn<sup>2+</sup> in g/L / Fe<sup>3+</sup> in g/L

## 5. RESULTS AND DISCUSSION

The aim of this work was to determine the densities and the oxygen solubilities in leach solutions at the conditions that simulate the conditions and solutions used in the zinc pressure leaching processes. In this chapter, the results for densities and solubilities are presented and discussed.

### 5.1 Oxygen Solubilities

The experimental data obtained were evaluated to find the effect of pressure and concentration on the solubilities of oxygen in the leach solutions. The solubilities determined in this work were the saturation or equilibrium solubilities. To make sure that the solutions in the absorption vessel were saturated, the time of absorption was increased until further increase in absorption time did not produce any difference in the solubility. On the other hand, complete desorption was ensured by reducing the flow rate of the solution in the desorption apparatus until further reductions in the flow rate for the same saturated solution did not change the amount of gas released. At least two determinations were made for each solution at each different condition of temperature and pressure. At 458 K (185°C) additional replicates were made

because there was some difficulty in obtaining as high a consistency in results as at 368 K (95°C). Several pairs of volumes of gas and solvent were fitted using a least squares relation to obtain the oxygen solubility in each solution at each condition and for each determination. The least squares relation described the linear relationship between the volumes of gas and volumes of solvent. Typical results are presented in Figure 4. The results show that the amount of gas released by the solvent of the same composition decreased with decreasing partial pressure of oxygen, that is the solubility is proportional to the oxygen partial pressure. Also, the volumes of gas released in all cases are relatively small compared to the volumes of their corresponding solvents. The amount of oxygen obtained by the method explained in the Experimental Procedure was the oxygen that was absorbed in excess of that dissolved at 101.3 kPa and 323 K. The solubilities of oxygen in these solutions at 101.3 kPa and 323 K were determined by Leung (Unpublished Data), by absorbing oxygen directly in degassed solutions.

A basic computer program was employed to calculate the mole fraction solubility, Henry's law constant and the oxygen solubility expressed in g/L for each solubility determination. Also, determined was the oxygen solubilities corresponding to an oxygen partial pressure of 0.1013 MPa (1 atm). An average Henry's constant and average gas solubilities corresponding to

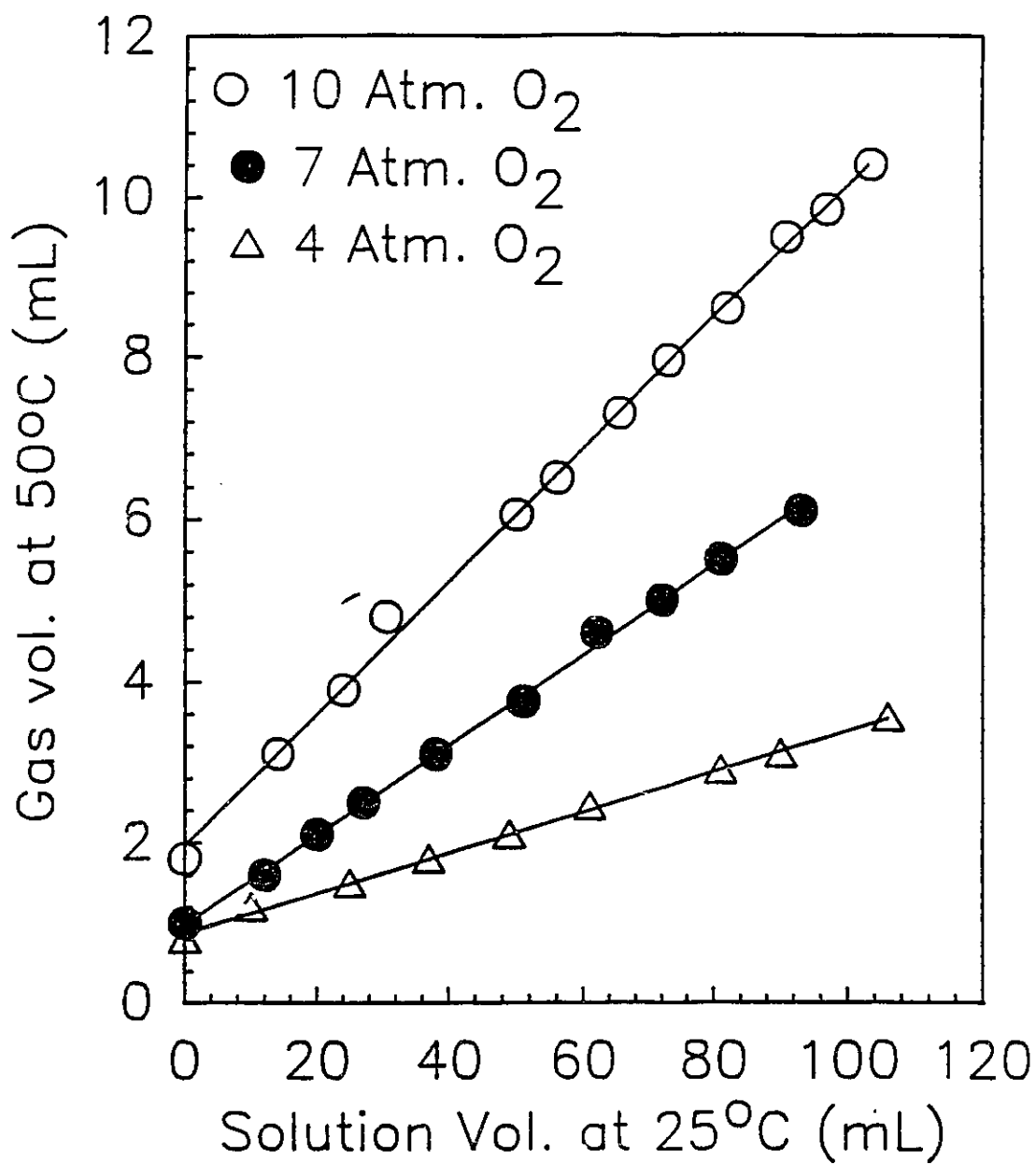


Figure 4. Plot of the Volumes of Gas versus Volumes of Solution for a Solution Containing 5 g/L Acid, 110 g/L Zinc and 1 g/L Iron at 368 K.

oxygen partial pressure of 0.1013 MPa were then calculated for each solution, each pressure and each temperature.

Typical results for oxygen solubilities in the acid leach solutions at the three pressures, 1.013, 0.7093 and 0.4053 MPa of oxygen are shown for a temperature of 398 K in Figure 5. It can be observed that the solubility increases linearly with an increase in the oxygen partial pressure. The fit is extremely good in all cases and the graph shown can be considered typical of all the data obtained. Data for other temperatures are presented in Appendix A. It is quite apparent from Figure 5 that the solubility behaviour of these solutions closely obeys Henry's law. This behaviour is usually observed for the solubilities of slightly soluble gases such as oxygen. Further, Figure 5 clearly indicates that the oxygen solubility in 5 g/L sulphuric acid solution is almost the same as in water. There is also a very large reduction in oxygen solubility in the solution corresponding to an increase in zinc concentration. For the solution containing 110 g/L of zinc, the oxygen solubility is only about 40% of that for the oxygen solubility in water or dilute (5 g/L) sulphuric acid solution. The reductions in oxygen solubilities as a result of increasing iron concentration and sulphuric acid concentration do not appear to be as large as those for increasing concentrations of zinc.

The average solubility results for oxygen are reported for an oxygen partial pressure of 0.1013 MPa in Table 2.

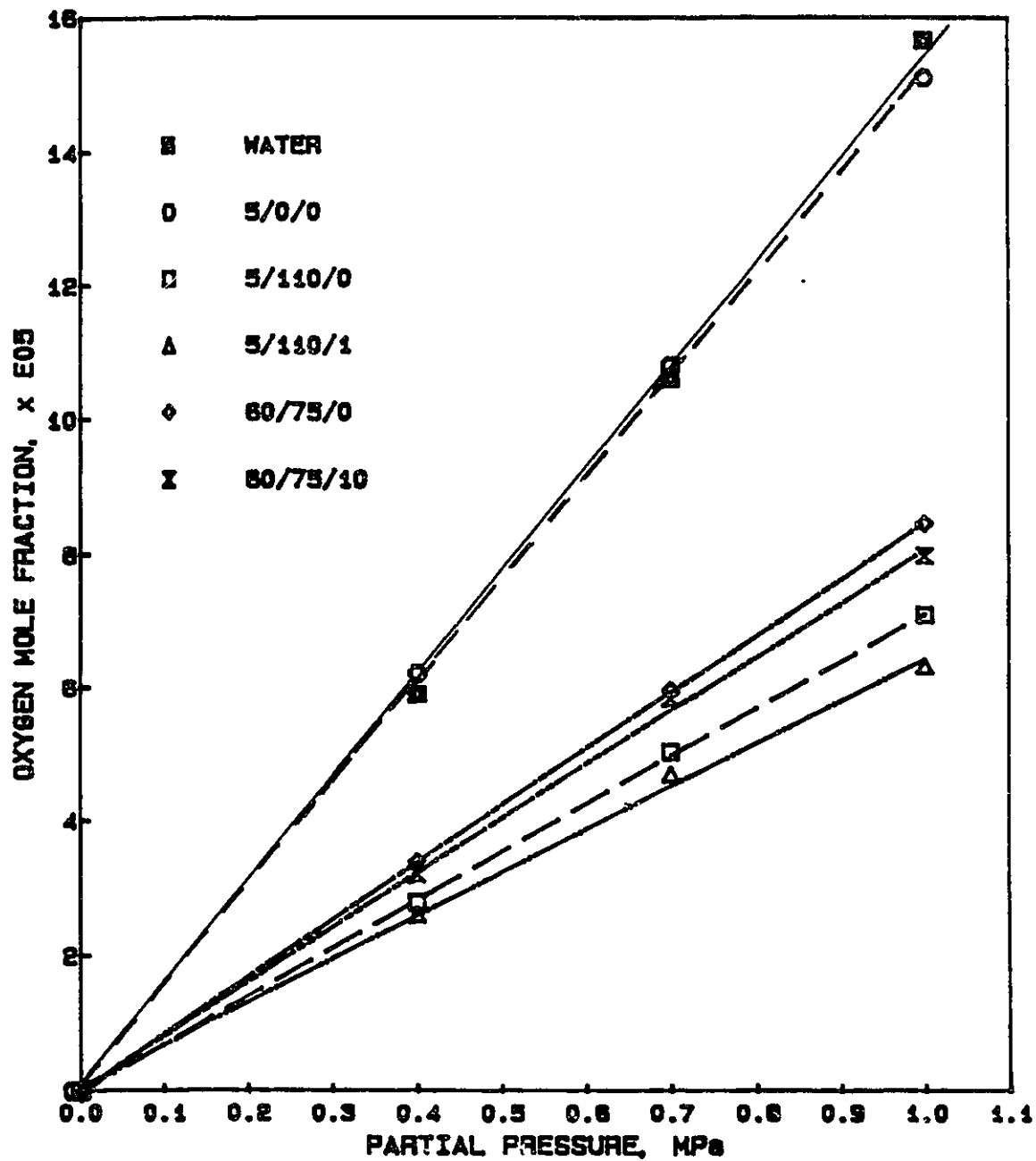


Figure 5. Mole Fraction Solubility of Oxygen in Aqueous Acid-Salt Solutions at 398 K

Table 2. Solubilities of Oxygen in the Leach Solutions

Temperature,						
K		323	368	398	428	458
Solution						
Water	$(10^{-3}) K_H$		70.59	65.86	54.47	43.65
	$(10^5) x$	1.697	1.417	1.518	1.836	2.291
	$(10^2) C_g$		2.510	2.690	3.250	4.055
	$(10^2) \alpha^0$		1.701	1.773	2.083	2.512
5/0/0	$(10^{-3}) K_H$		73.75	63.90	53.77	43.82
	$(10^5) x$	1.640	1.356	1.535	1.860	2.282
	$(10^2) C_g$		2.400	2.717	3.290	4.036
	$(10^2) \alpha$		1.624	1.795	2.116	2.510
	$(10) k_{sca}$		3.945	-1.050	-1.339	0.06783
5/110/0	$(10^{-3}) K_H$		178.5	140.5	106.4	69.33
	$(10^5) x$	0.820	0.5602	0.7117	0.9429	1.443
	$(10^2) C_g$		1.007	1.279	1.695	2.593
	$(10^2) \alpha$		0.6835	0.8463	1.092	1.617
	$(10) k_{sca}$		2.285	1.853	1.619	1.098
5/110/1	$(10^{-3}) K_H$		181.6	154.0	103.4	64.21
	$(10^5) x$	0.820	0.5505	0.6495	0.9667	1.557
	$(10^2) C_g$		0.9897	1.168	1.738	2.800
	$(10^2) \alpha$		0.6707	0.7712	1.119	1.743
	$(10) k_{sca}$		2.320	2.075	1.548	0.9111
60/75/0	$(10^{-3}) K_H$		133.0	117.1	95.00	58.51
	$(10^5) x$	0.800	0.7516	0.8542	1.053	1.709
	$(10^2) C_g$		1.325	1.506	1.855	3.013
	$(10^2) \alpha$		0.8956	0.9920	1.192	1.877
	$(10) k_{sca}$		1.584	1.434	1.378	0.7199
60/75/10	$(10^{-3}) K_H$		148.6	123.3	100.1	59.76
	$(10^5) x$	0.700	0.6729	0.8107	0.9993	1.673
	$(10^2) C_g$		1.109	1.423	1.754	2.936
	$(10^2) \alpha$		0.7991	0.9393	1.132	1.837
	$(10) k_{sca}$		1.776	1.494	1.433	0.7354

Using Henry's law, oxygen solubilities at various pressures can be obtained as a simple factor of that at 0.1013 MPa expressing the actual oxygen pressure in MPa.

The results of oxygen solubility in water at all temperatures were found to be consistently higher than the previously reported values from the literature. At 368 K the recommended oxygen solubility in mole fraction is  $1.403 \times 10^{-5}$  (Battino, 1981) whereas the value obtained in this work was  $1.417 \times 10^{-5}$ . The difference between the two is about 1%. This small difference suggests that the equipment and procedure give accurate solubility results. However, the difference increases progressively with temperature and reaches about 4% at 458 K. It is difficult to obtain accurate solubilities at high temperatures and for the resulting high vapour pressures of the solutions. For example, in his analysis of oxygen solubility in water at temperatures above 373 K, Battino used a single study carried out by Stephan et al. (1956). To ensure that results of high consistency were obtained, measurements at 458 K were repeated three or four times. Furthermore, because the measurements were made at three different pressures, an automatic check of the consistency of the results was obtained. Also, in most cases, errors in solubility determination tend to give lower values of gas solubilities. For these reasons it is suggested that the results obtained in this work are probably more accurate than those appearing in the literature.

Unlike the effect of pressure and which is expressed very well by Henry's law, the effect of temperature on solubility is more complex. An analysis of gas solubilities in water was reported by Hayduk and Laudie (1973). In their paper they showed that solubilities of a number of slightly soluble gases in water have minima. There is a minimum solubility of oxygen in water at a temperature of about 373 K. The solubility increases markedly at higher and lower temperatures. Further, they explained that the increase in solubility above 373 K was probably due to the weakening of the hydrogen bonds in water at temperatures above 373 K. It has been experimentally observed for water and non aqueous solvents alike that gas solubilities pass through a minimum and then increase as the temperature rises (Prausnitz and Lichtenthaler, 1986). Some thermodynamic explanation for this phenomenon is given by Beutier and Renon (1978), Schotte (1985), Japas and Sengers (1989) and Harvey and Sengers (1990). Similar oxygen solubilities are observed for water and the dilute acid solution as shown in Figure 6. Comparable, but not identical, solubility relations are observed for the oxygen solubilities in the acid-salt leach solutions used in this work. All the electrolytes used, sulphuric acid, iron sulphate and zinc sulphate, caused a decrease in the solubility of oxygen as compared to the solubilities in water. At lower and moderate temperatures (323-428 K) the solubilities are very much reduced by these electrolytes, but at the higher temperature

(458 K) the oxygen solubilities approach the solubilities of oxygen in water. This tendency can be clearly seen by looking at the variation of the Setschenow salt effect parameters presented in Table 2. These values were calculated using the total electrolyte concentration of each solution and the Bunsen coefficient in water obtained at the corresponding conditions. The Setschenow salt effect parameter for each solution decreases with an increase in temperature. This is equivalent to saying that oxygen is salted out by the sulphuric acid-salt leach solutions. Only the dilute sulphuric acid was found to salt in the oxygen slightly.

The salting out is more pronounced at lower temperatures. At higher temperatures, the salting out decreases and the solubilities increase. The decrease of the salting out with increase in temperature is not uniform and varies from one solution to another. For example, there is a gradual increase in the oxygen solubilities in these solution from 368 to 428 K. This is followed by a sudden and sharp increase in solubility from 428 to 458 K. For this reason there is no well-defined minima for the solubility of oxygen in solutions containing different quantities of zinc, iron and sulphuric acid.

In Figure 6, an unexpected trend is observed for the solution containing 5 g/L acid, 110 g/L zinc and 1 g/L iron. At lower temperatures this solution has oxygen solubilities that are smaller than those in the solution containing 5 g/L

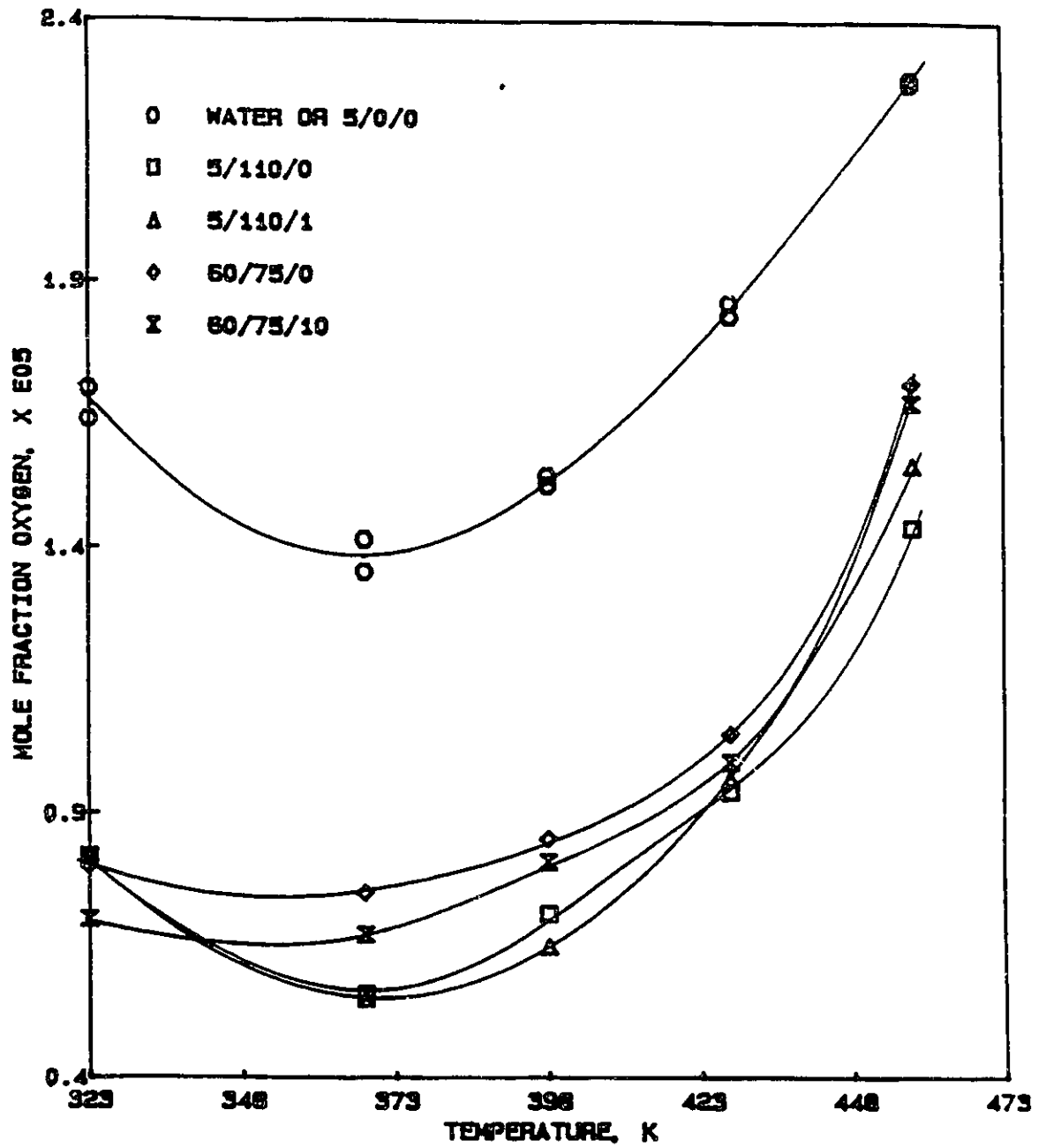


Figure 6. Mole Fraction Solubility of Oxygen in Aqueous Sulphuric Acid-Salt Solutions for a Partial Pressure of 101.3 kPa

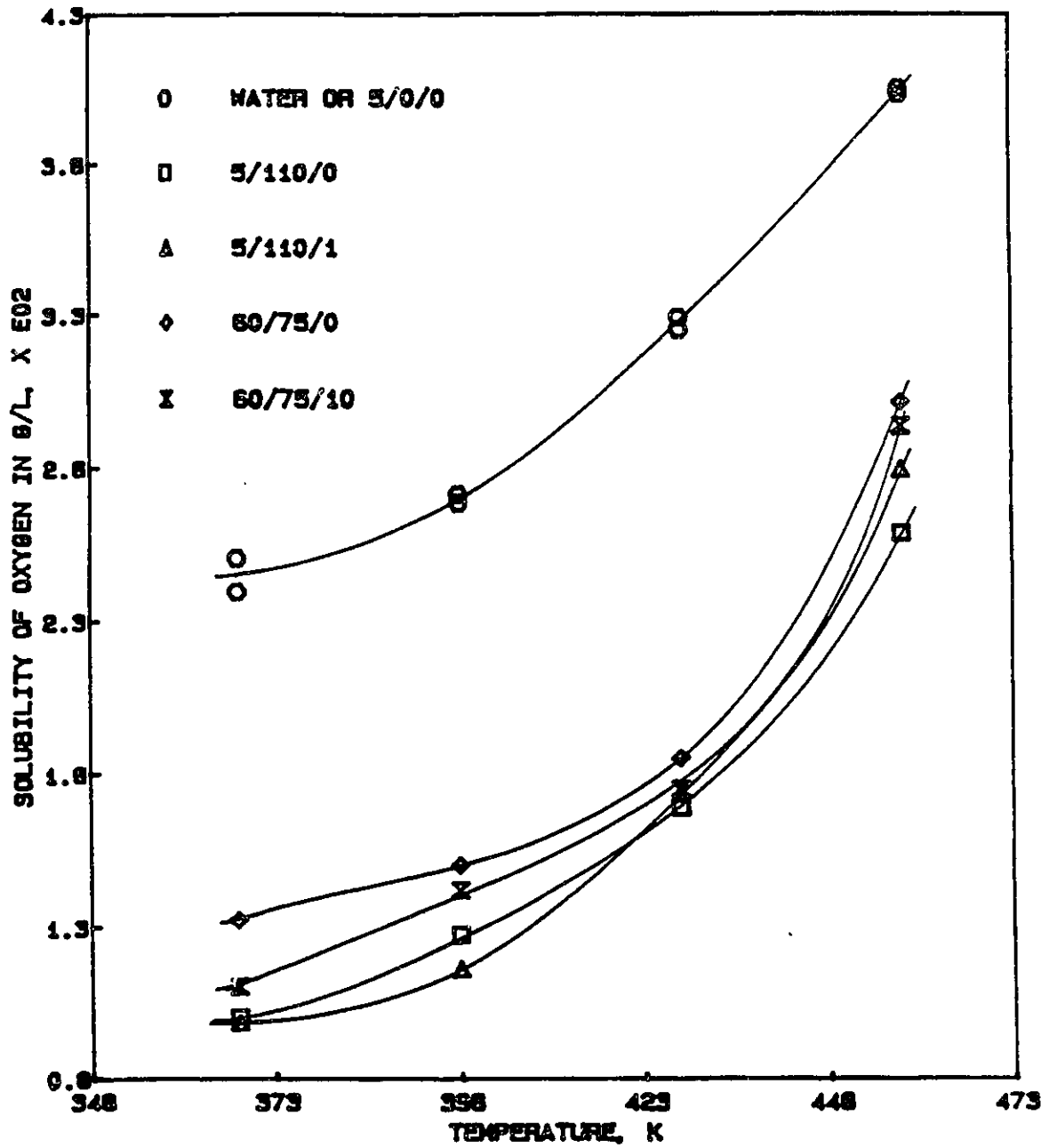


Figure 7. Solubility of Oxygen in g/L in Aqueous Sulphuric Acid-Salt Solutions for a Partial Pressure of 101.3 kPa

and 110 g/L zinc without iron. However, at higher temperatures the oxygen solubilities in the former solution are higher at the same conditions of temperature and pressure. Experimental observation indicated that there was a formation of a reddish brown precipitate (probably of a complex iron salt) in the solution that contained 1 g/L iron at temperatures of 428 and 458 K. Similar precipitates are reported in the actual pressure leaching process for leach processes conducted under low acidity (Chalkley and Weir, 1983), where the precipitates are caused by the formation of plumbojarosite ( $\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$ ). If it was only the ferric sulphate that was precipitated, one would have expected that the oxygen solubility in the two solutions to be the same. The fact that the oxygen solubilities are higher in the solution which initially had a higher concentration of electrolytes, suggests that the precipitates contained electrolytes other than the ferric sulphate. This would have reduced the concentration of the solution below the concentration of the solution that contained no iron and the increase in the oxygen solubilities could be justified.

The salting out effect mentioned above and its variation with temperature and concentration can be observed in Figures 6 and 7, which show the oxygen solubilities expressed in mole fraction, and in g/L, respectively. The solubilities calculated as g/L of oxygen at an oxygen partial pressure of 101.3 kPa are reported for volumes of solution as if their

volumes were measured at 298 K (25°C) even though the actual experiments were conducted at much higher temperatures. This procedure makes it much easier to make direct comparisons with solubilities of oxygen in water and other solutions at ambient conditions. The units of g/L for expressing gas solubilities are not very common in the technical literature but are commonly used by technical personnel in the metallurgical industries.

In section 3.1 it was explained that in order to perform experiments at 428 K and 458 K for the solution containing 60 g/L acid and 75 g/L without iron, 2 g/L of iron were added in the form of ferric sulphate. The effect of this addition will now be discussed. It is noted that the solubilities of oxygen were measured in the solutions containing sulphuric acid, zinc and ferric ions in the proportions expressed in g/L of 5,110,0 and 5,110,1. The addition of 1 g/L of ferric ion to the latter solution, while producing negligible changes in the oxygen solubility at lower temperatures, did not give any reasonable comparison because of the formation of precipitates at higher temperatures, as explained before. However, a quantitative estimate of the effect of the addition of 2 g/L of ferric ion can be found by comparing the results for the 60,75,2 and the 60,75,10 g/L acid, zinc, ferric ion solutions. The difference in the oxygen solubilities between the two solution at 458 K is  $0.0359 \times 10^{-5}$  mole fraction. This would correspond to a 0.53% decrease in solubility for the addition

of 2 g/L of ferric ion. While this amount is not a totally negligible effect on the oxygen solubility, this possible deviation is within the experimental error. Thus, this method is considered to give satisfactory solubility results. In addition, of course, it was essential to use such an approach to obtain solubilities in these solutions at all.

The precision of the solubility results was estimated. Solubility measurements using absorption methods alone when done with care can still contain errors of up to 2%. In this case two consecutive operations are required for the determination of each solubility. First, the absorption step at high pressure and temperature and second, the desorption step at atmospheric pressure and 323 K. It is considered that each of these steps has a potential experimental error of 2 % and hence the overall experimental error is the addition of the two or 4%. Results for 368 K had a high degree of reproducibility and had probable errors of less than 2% while results at higher temperatures were increasingly less reproducible until at 458 K, where the probable errors may have been greater than 2%. Thus a realistic estimate of the overall experimental error for these results is  $\pm 4\%$ .

## 4.2 Densities of Solutions

The densities of the acid-salt leach solutions were measured at 298 and 323 K using the precision vibration-reed density meter. At temperatures of 368 to 458 K, the measurements were carried out in dilatometers where the dilations of the solution inside the pyrex glass capillary tubes were accurately measured by using a cathetometer as the temperature was increased. Three determinations were made for each solution at each temperature. Densities were calculated from the readings of the vibrating frequency obtained with the density meter and the lengths of the solutions in the dilatometers at each temperature. The experimental results of densities in  $\text{kg/m}^3$  are presented in Table 3. The maximum experimental error for the densities has been estimated to be  $\pm 0.2\%$  based on the precision of the measurements of dilation. The densities measured by using the density meter have a higher accuracy of about  $\pm 0.05\%$ .

Except for water, there were no densities for direct comparison with those of the solutions used here. Water was used for calibration of the dilatometers and experiments were carried out in triplicate. A small error for each capillary tube of less than 1.0% was found because of the expansion of the tubes and a small correction factor for each was required. Because of the high viscosity of ethylene glycol, it could not be used successfully because it was difficult to charge into

**Table 3. Densities of the Solutions in kg/m<sup>3</sup> at Experimental Conditions**

Temperature,						
K	298	323	368	398	428	458
Solution						
Water	997.1	988.0	965.3	939.1	912.3	881.6
5/0/0	1001	991.8	966.7	943.9	918.2	887.9
5/110/0	1256	1245	1217	1186	1155	1118
5/110/1	1261	1247	1220	1189	1159	1121
60/75/0	1206	1193	1164	1134	1107	1073
60/75/10	1236	1224	1194	1165	1139	1104

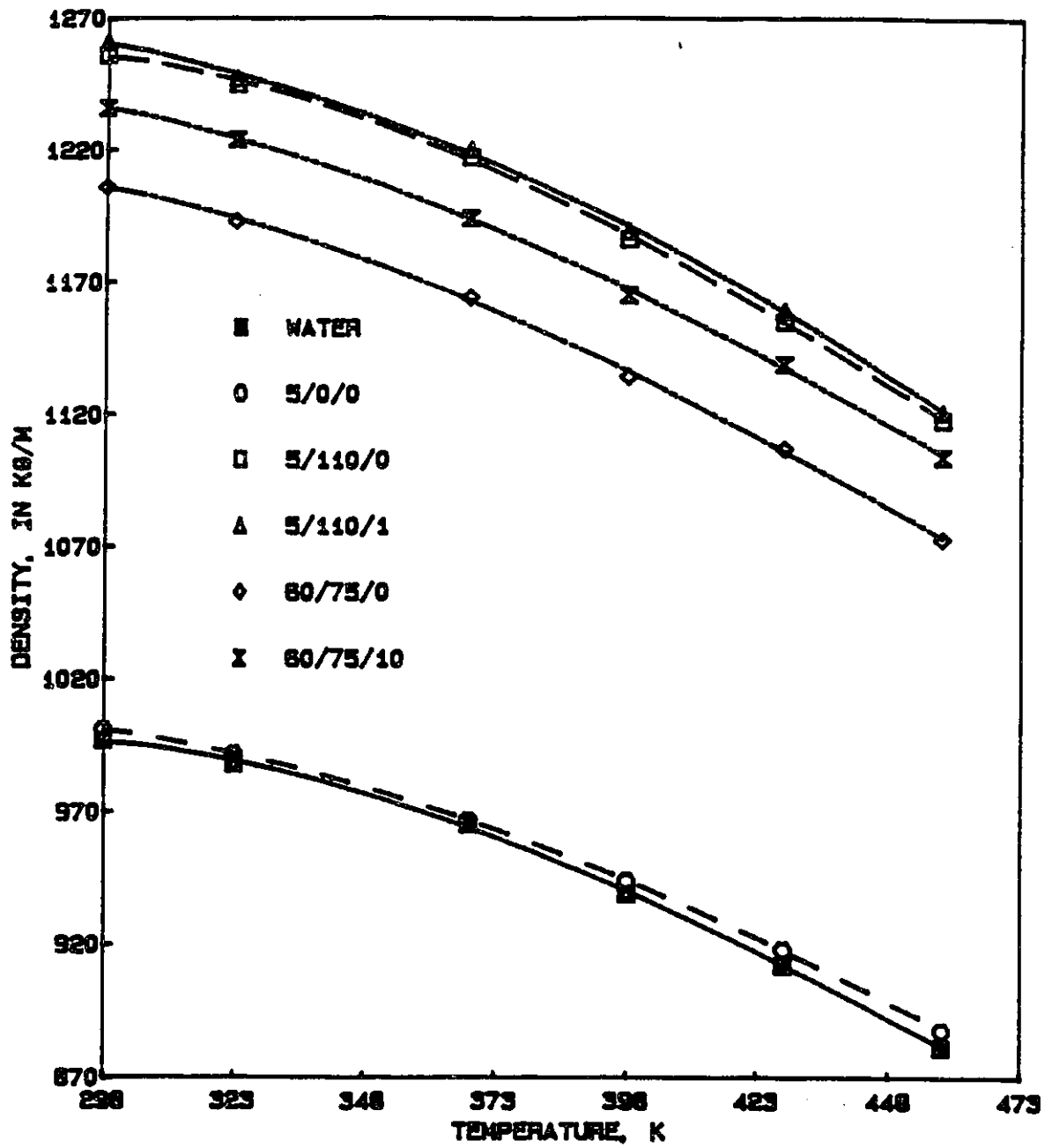


Figure 8. Densities of Acid-Salt Solution at the Experimental Conditions of Temperature and Pressure.

the capillary tubes and subsequently to completely remove it from the tubes after measurements. For these reasons ethylene glycol, which has known densities in the temperature range of this work, could not be used to give a possible additional corroboration of the densities. However, in view of the good agreement between consecutive measurements for water and all the solutions, the dilatometer apparatus is considered reliable and the results are considered satisfactory.

The results for densities of the solutions at the experimental temperatures are also shown in a graphical form in Figure 8. It can be observed from Figure 8 that, as expected, the densities decrease with increase in temperature. While the decrease is small at lower temperatures it becomes significantly large at high temperatures. This behaviour is expected because of the usual increase of volumes of liquids caused by thermal expansion as they are heated up. The decrease in densities of the solutions followed the same pattern as that of the density of water.

The effect of concentration of the electrolytes on the densities is also shown in Figure 8. The densities increase with an increase in salt or acid concentration. However, the effect of zinc and iron concentrations seems to be larger than that for sulphuric acid. For example, for the solution containing 110 g/L zinc, 5 g/L acid and 1 g/L iron, the density is about 27% higher than that of pure water. As explained before, this solution also produced some reddish

brown precipitates during the density determination at 428 and 468 K. However, in this case there is no evidence that the precipitates affected the overall density of the solution at these temperatures. The density remained higher than that of the corresponding solution which contained no iron and continued to follow the same pattern as for the rest of the solutions in spite of the occurrence of the precipitation.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 Conclusions

1. The solubilities of oxygen in the aqueous sulphuric acid - zinc and iron salt leach solutions closely obey Henry's law.
2. As the temperature is increased from 368 to 458 K, there is generally a large increase in the solubilities of oxygen in the aqueous sulphuric acid-zinc and iron salt leach solutions.
3. A marked reduction in the oxygen solubilities is observed at all temperatures as the quantity of dissolved zinc sulphate is increased in the solution.
4. In general, increasing quantities of dissolved sulphuric acid and iron sulphate also cause a decrease in oxygen solubilities in the leach solutions.
5. The effect of the precipitation of iron salt from a solutions with low acidity at higher temperatures is to increase the oxygen solubility in those solutions.
6. The use of ferric ions is an effective way of controlling the corrosion of titanium by the leach solutions at temperatures exceeding 423 K (150°C).

7. A two-step, absorption-desorption procedure is a practical way for determining solubilities in the leach solutions at high pressures and temperatures.

8. In the temperature and pressure ranges investigated, the densities of the solutions decrease as the temperature is increased following the same pattern as that for pure water, and increase with an increase in concentration of iron, zinc and/or sulphuric acid.

9. The use of dilatometers for determining the densities of the solutions at high temperatures and pressures is reliable and practical.

## 6.2 Recommendations

1. The actual vapour pressure of the solutions should be measured at the operating conditions to avoid the use of estimated values.

2. Steps should be taken to improve the pressure range of the solubility equipment so that the same partial pressures of oxygen could be used at all temperatures.

3. Other tubing materials such as lead should also be tried

in looking for the possibility of using materials that can withstand corrosion without the use of ferric or copper ions.

4. For convenience, the use of an oil bath with more depth is recommended in density determination so that straight dilatometer tubes may be used.

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**APPENDIX A: EXPERIMENTAL DATA**

**Table 4. Average Oxygen Solubilities at 368 K in (10<sup>5</sup>).Mole Fraction**

Pressure of oxygen, MPa	0.4053	0.7093	1.013
Solution			
Water	5.581	10.07	14.16
5/0/0	5.441	9.606	13.19
5/110/0	2.249	3.971	5.520
5/110/1	2.256	3.842	5.449
60/75/0	2.994	5.224	7.602
60/75/10	2.747	4.586	6.871

**Table 5. Average Oxygen Solubilities at 398 K in (10<sup>5</sup>).Mole Fraction**

Pressure of oxygen, MPa	0.4053	0.7093	1.013
Solution			
Water	5.902	10.61	15.66
5/0/0	6.221	10.81	15.11
5/110/0	2.798	5.029	7.109
5/110/1	2.620	4.691	6.332
60/75/0	3.402	5.970	8.471
60/75/10	3.205	5.830	7.990

**Table 6. Average Oxygen Solubilities at 428 K in (10<sup>5</sup>).Mole Fraction**

Pressure of oxygen, MPa	0.4053	0.7093	1.013
Solution			
Water	7.348	13.31	17.94
5/0/0	7.264	13.32	18.67
5/110/0	3.714	6.538	9.671
5/110/1	3.670	6.904	9.914
60/75/0	4.0752	7.879	10.08
60/75/10	3.987	6.972	10.05

**Table 7. Average Oxygen Solubilities at 458 K in (10<sup>5</sup>).Mole Fraction**

Pressure of oxygen, MPa	0.2027	0.4053	0.7093
Solution			
Water	4.787	8.854	15.87
5/0/0	4.615	9.018	15.96
5/110/0	2.945	5.925	9.617
5/110/1	3.271	6.223	10.37
60/75/0	3.485	7.146	11.41
60/75/10	3.621	6.958	11.26

**Table 8. Average Vibrating Frequency Readings Obtained with the Density Meter**

Solution	Temperature, K	298	323
Water		97492	97172
Ethylene Glycol		100142	99625
5/0/0		97587	97264
5/110/0		103199	103192
5/110/1		103620	103234
60/75/0		102383	101996
60/75/10		103066	102706

**Table 9. Lengths of Solutions in the Dilatometer Tubes in m**

Temperature, K		323	368	398	425	458
Solution	Tube					
Water	1	0.38285	0.39280	0.40217	0.41389	0.42714
	2	0.37085	0.37975	0.38855	0.39949	0.41234
	3	0.37875	0.38853	0.39756	0.40843	0.42260
	4	0.40477	0.41521	0.42498	0.43737	0.45230
5/0/0	4	0.40130	0.41171	0.42076	0.43280	0.44768
	4	0.38270	0.39263	0.40126	0.41212	0.42516
5/110/0	4	0.40838	0.41820	0.42743	0.43926	0.45312
	1	0.37627	0.38537	0.39377	0.40415	0.41722
	1	0.35671	0.36582	0.37379	0.38358	0.39481
5/110/1	3	0.37502	0.38449	0.39239	0.40297	0.41508
	3	0.36680	0.37606	0.38379	0.39446	0.40705
	2	0.36639	0.37474	0.38251	0.39133	0.40193
60/75/0	2	0.36395	0.37332	0.38102	0.39037	0.40154
	2	0.36021	0.36994	0.37757	0.38730	0.39850
	4	0.40325	0.41405	0.42268	0.43309	0.44478
60/75/10	1	0.38060	0.39079	0.39892	0.40824	0.41988
	1	0.38491	0.39522	0.40345	0.41236	0.42416
	4	0.39764	0.40872	0.41666	0.42592	0.43728

**Table 10. Average Correction Factors for Expansion of Dilatometer Tubes**

Temperature, K	323	368	398	425	458
Tube					
$\rho_{act}, \text{ kg/m}^3$	988.0	965.3	939.1	912.3	881.6
1. $\rho_{me}, \text{ kg/m}^3$		965.3	939.1	912.3	881.6
r		1.002336	0.99838	0.99824	0.99548
2. $\rho_{me}, \text{ kg/m}^3$		964.9	943.0	917.2	888.6
r		1.000383	0.99582	0.99469	0.99212
3. $\rho_{me}, \text{ kg/m}^3$		963.2	941.3	916.2	885.5
r		1.00216	0.99763	0.99573	0.99560
4. $\rho_{me}, \text{ kg/m}^3$		963.2	941.1	914.4	884.2
r		1.00213	0.99789	0.99774	0.99706

**Table 11. Corrected Average Lengths of Solutions in Dilatometer  
Tubes in m**

Temperature, K	323	368	398	425	458
Solution					
5/0/0	0.39078	0.40093	0.41061	0.42210	0.43651
5/110/0	0.38285	0.39166	0.40190	0.41268	0.42634
5/110/1	0.37030	0.37870	0.38857	0.39863	0.41214
60/75/0	0.40477	0.41485	0.42583	0.43622	0.45004
60/75/10	0.37875	0.38827	0.39793	0.40701	0.41992

**Table 12. Additional Data: Number of Moles in a Litre of Solution,  $n_1$ , and Total Mole Concentration of the Electrolytes,  $C_2$ , at 298 K**

Solution	<u>Total solution</u>	<u>Electrolyte only</u>
	$n_1$ , mol/L	$C_2$ , mol/L
5/0/0	55.32	0.051
5/110/0	56.18	1.733
5/110/1	56.18	1.742
60/75/0	55.08	1.758
60/75/10	54.84	1.848

## APPENDIX B: SAMPLE CALCULATIONS

### B1. Preparation of Solutions

Sample calculations of the amounts of chemicals used to prepare the test solutions are shown. In all calculations, the 60 g/L sulphuric acid solution with 75 g/L zinc and 10 g/L iron was taken as an example and a basis of 1000 mL of solution was used.

#### B1.1 Amount of Sulphuric Acid

The amount of sulphuric acid required was calculated from the density of the sulphuric acid and its specified percentage purity.

Example: In the solution specified above, 60 grams of pure sulphuric acid were required. The density of the acid was 1840 kg/m<sup>3</sup> and the percentage purity was 96%.

It means that, 1 m<sup>3</sup> of the 96% acid contains

$$1\text{m}^3 * \frac{96}{100} * 1840\text{kg/m}^3 = 1766.4\text{kg of pure sulphuric acid}$$

Therefore, 0.06 kg of pure acid can be obtained from:

$$\left(\frac{1\text{m}^3}{1766.4\text{kg}}\right) 0.06 = 3.3967 * 10^{-5} \text{m}^3 = 33.97\text{mL of sulphuric aci.}$$

#### B1.2 The Amount of Zinc Sulphate

The amount of zinc sulphate required was obtained by using the molecular weight of the hydrated zinc sulphate and the atomic mass of zinc and the specified purity.

**Example:** In the solution mentioned before, 75 grams of zinc were needed. The molecular weight of the hydrated zinc sulphate was 287.58 kg/kmol, the atomic mass of zinc is 65.38 and the purity was 99.5%.

Therefore, 65.38 kg of zinc are contained in:

$$\frac{1 \text{ kmol} * 287.58 \text{ kg/kmol}}{\frac{99.5}{100}} = 289.0 \text{ kg of powder.}$$

To get 0.075 kg of zinc, the amount of powder needed:

$$\frac{289.0 \text{ kg/kmol}}{65.38 \text{ kg/kmol}} * 0.075 \text{ kg} = 0.32989 \text{ kg} = 32.989 \text{ g}$$

### B1.3 Amount of Iron Sulphate

The amount of the hydrated ferric sulphate powder required was calculated from the molecular weight of the anhydrous ferric sulphate, the percentage of the anhydrous ferric sulphate and the atomic weight of iron.

**Example:** The molecular weight of ferric sulphate is 399.88 kg/kmol and the percentage of ferric sulphate in the salt was 73.2%. The atomic mass of iron is 55.85 and there are two atoms of iron per molecule of ferric sulphate.

Therefore, 111.70 kg of iron were obtained from:

$$1 \text{ kmol} * 399.88 \text{ kg/kmol} * 100/73.2 = 546.3 \text{ kg of powder}$$

To get 0.01 kg, the amount of the powder needed was:

$$546.3 \text{ kg} * \frac{0.01 \text{ kg}}{111.70 \text{ kg}} = 0.04891 \text{ kg} = 48.91 \text{ g of powder}$$

## B2. Vapour Pressure of Solutions

The vapour pressures of aqueous sulphuric acid solutions were estimated by using Fig 9.

**Example:** The vapour pressure of a 60 g/L sulphuric acid solution (mass fraction 5.79%) is estimated from Figure 9 to be 0.8164 MPa (0.8057 atm).

The vapour pressures of the other solutions were then estimated using Equation (24). The effects of two or more salts on the vapour pressure was considered to be additive. The activity coefficients for zinc sulphate and iron sulphate were evaluated by comparing the vapour pressures estimated by using the actual Raoult's law, Equation (19) and the measured values available in the literature (Weast, 1986).

**Example:** A solution of 0.5 moles of  $\text{ZnSO}_4$  in a litre of water at  $100^\circ\text{C}$  reduces the vapour pressure by 4.9 mm Hg.

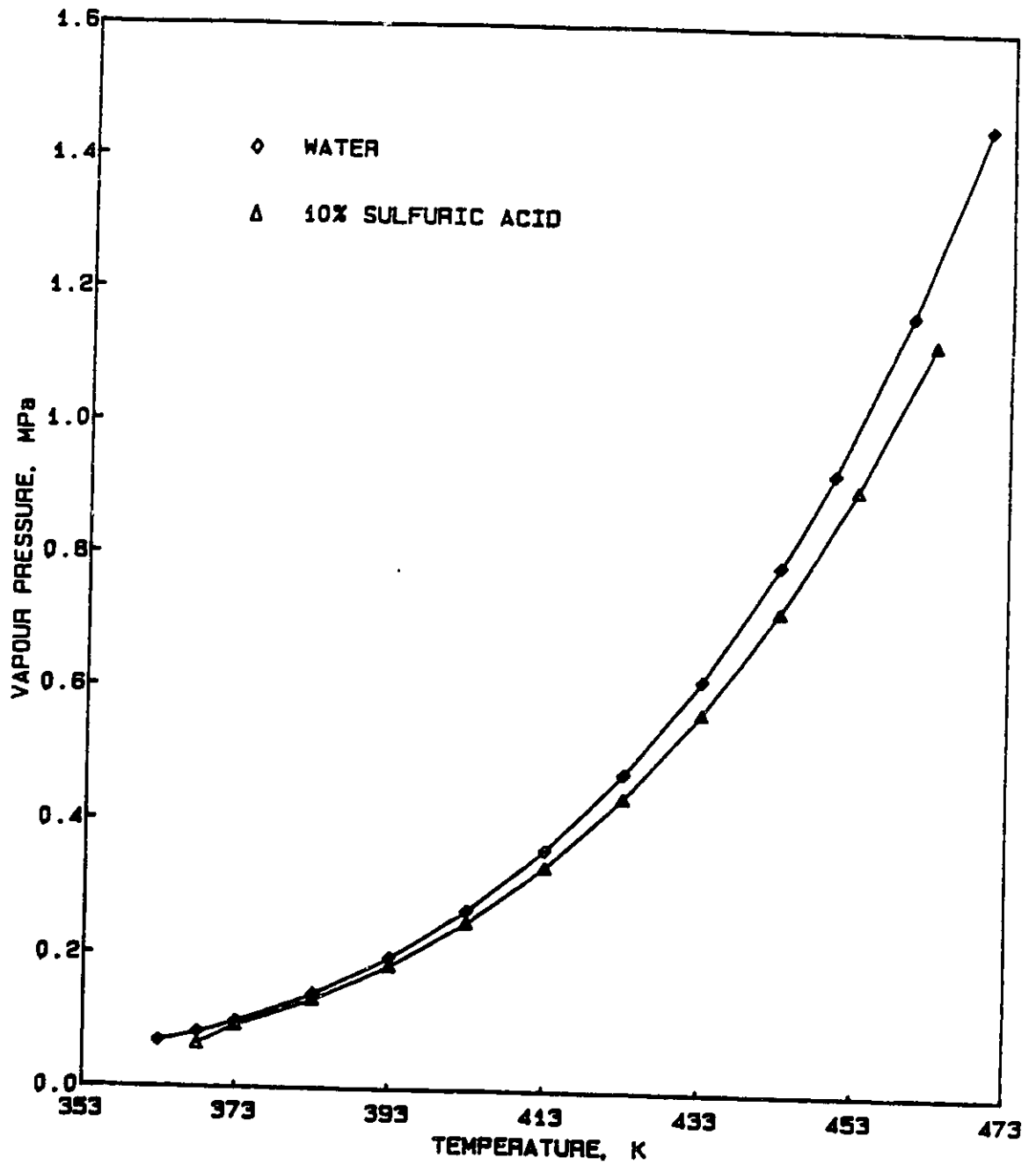


Figure 9. Vapour Pressure of Water and 10% Aqueous Sulphuric Acid Solution

The number of moles of water in a litre at 100°C = 957.9/18.02  
= 53.16

$$\therefore \text{mole fraction } \text{ZnSO}_4 = \frac{0.5}{(53.16 + 0.5)} = 0.00932$$

Using Equation (19)

$$p = p^\circ * (0.0932) = 760 \text{ mmHg} * 0.00932 = 7.08 \text{ mmHg}$$

$$\therefore \gamma_{\text{ZnSO}_4} = \frac{4.9}{7.08} = 0.692$$

Similarly for  $\text{FeSO}_4$

$$\gamma_{\text{ZnSO}_4} = \frac{5.8}{7.08} = 0.819$$

The activity coefficients above are used in Equation (24).

$$P = P^\circ * (\gamma_{\text{ZnSO}_4} X_{\text{ZnSO}_4} + \gamma_{\text{Fe}_2(\text{SO}_4)_3} X_{\text{Fe}_2(\text{SO}_4)_3})$$

**Example:** In a solution of 60 g/L  $\text{H}_2\text{SO}_4$  with 75 g/L  $\text{Zn}^{2+}$ , and 10 g/L  $\text{Fe}^{3+}$ , the mass fraction of the salts are 0.0209, and, 0.00185, respectively. The vapour pressure at 90°C is:

$$\begin{aligned} p &= 0.8057 \text{ MPa} (0.692 (0.0209) + 0.819 (0.00185)) \\ &= 0.8033 \text{ MPa (or } 0.7928 \text{ atm)} \end{aligned}$$

### B3. The Bunsen Coefficient

The Bunsen coefficient was calculated from Equation (17). The volume of gas at STP, ( $V_{(g)}$ ) was calculated from the mole

fraction of oxygen by multiplying the mole fraction by the total number of moles in a litre of solution saturated with oxygen, and the oxygen molar volume at STP.

**Example:** At 95°C the mole fraction of oxygen in the solution specified above is  $0.6729 \times 10^{-5}$ . A volume of 1 m<sup>3</sup> of this solution contains 54.84 kmol. The volume of the gas at 273 K and 101.325 kPa is:

$$\begin{aligned} V_{(g)} &= 0.6729 \times 10^{-5} \times 22.414 \times 10^{-3} \text{ m}^3/\text{kmol} \times 54.84 \text{ kmol} \\ &= 8.271 \times 10^{-6} \text{ m}^3 \end{aligned}$$

The volume of the solution which absorbed this volume of gas at the temperature of absorption, is obtained by the ratio of the density of that solution at 25°C (volume of solution of 1 m<sup>3</sup>) to the density at the temperature of absorption.

**Example:** A volume of 1 m<sup>3</sup> of the solution mentioned above at 25°C will increase when heated to 95°C to:

$$V_L = 1 \text{ m}^3 \times \frac{\rho_{25^\circ}}{\rho_{95^\circ}} = 1 \text{ m}^3 \times \frac{1.236 \text{ kg/m}^3}{1.194 \text{ kg/m}^3} = 1.0352 \text{ m}^3$$

Therefore, for this solution the Bunsen coefficient at 95°C is:

$$\frac{8.271 \times 10^{-6}}{1.0352 \times 10^{-3}} = 0.007991$$

#### B4. The Setschenow Salt Effect Parameter

The Setschenow salt effect parameter is calculated from the logarithm of the Bunsen coefficient ratio and the reciprocal of the total concentration of the electrolytes in

solution.

Example: The Bunsen coefficients, for the solution used before, and water, at 95°C are (from Table 2) 1.701, and 0.7991, respectively. The total electrolyte concentration (from Table 12) is 1.848 kmol/m<sup>3</sup>. Therefore, the Setschenow salt effect parameter is:

$$k_{sca} = \frac{\log(1.701/0.7991)}{1.848 \text{ kmol/m}^3} = 0.1776 \text{ m}^3/\text{kmol}$$

## B5. Densities of Solutions

The densities were calculated using the values obtained from the density meter using Equation (35).

Example: At 25°C readings of vibrating frequency for water, and ethylene glycol were 100142, and 97492, respectively, and their corresponding densities at this temperature are 1109 and 997.1 kg/m<sup>3</sup>.

Using equation (35):

$$K = \frac{\rho_E - \rho_W}{\tau_E^2 - \tau_W^2} = \frac{(1109 - 997.1) \text{ kg/m}^3}{100142^2 - 97492^2} = 2.138 * 10^{-7} \text{ kg/m}^3$$

For the solution specified before, which had a reading from the density meter of 103066 at 25°C, the density is:

$$\begin{aligned} \rho &= \rho_E + K(\tau^2 - \tau_E^2) \\ &= 1109 \text{ kg/m}^3 + 2.138 * 10^{-7} \text{ kg/m}^3 (103066^2 - 100142^2) \end{aligned}$$

$$= 1236 \text{ kg/m}^3$$

Calculations of densities from the dilations measurements were carried out by using Equation (38).

Example: The solution used before had a length of 0.38912 m at 50°C and its average corrected length at 95°C was 0.39890 m. Its density at 25°C is 1224 kg/m<sup>3</sup>. Therefore, the density of this solution at 95°C is:

$$\rho = \frac{0.38912 \text{ m}}{0.39890 \text{ m}} * 1224 \text{ kg/m}^3 = 1194 \text{ kg/m}^3$$

## APPENDIX C

### A Basic Computer Program for Calculating the Solubilities

```
      HIGH PRESSURE SOLUBILITY OF OXYGEN IN LEACH SOLUTIONS
      FILE NAME IS OXSOL.BAS
      SOLUTION IS K = ACID G/L; L = ZINC G/L; M = IRON G/L
10    LPRINT "HIGH PRESSURE SOLUBILITY OF OXYGEN "
20    LPRINT "IN LEACH SOLUTIONS"
30    LPRINT "FILE NAME IS OXSOL.BAS"
40    LPRINT "SOLUTION IS K=ACID G/L; L=ZINC G/L; M=IRON G/L"
50    PRINT "INPUT K, L, M"
55    INPUT K,L,M
60    LPRINT "K =" ; K; "L =" ; L; "M =" ; M
130   INPUT "INPUT J =' ;J
140   DIM G(J), S(J), RHS(J), D(J), PD(J)
150   SS = 0
160   SG = 0
170   N = 0
180   SSS = 0
190   SGG = 0
200   SGS = 0
210   LPRINT
220   FOR I = 1 TO J
230   READ G(I), S(I)
250   SS = SS + S(I)
260   SSS = SSS + S(I) * S(I)
```

```

270 SG = SG + G(I)
280 SGG = SGG + G(I) * G(I)
290 SSG = SSG + S(I) * G(I)
300 N = N + 1
310 NEXT I
320 A = (SG * SSS - SS * SSG)/(N * SSS - SS * SS)
330 B = (N * SSG - SS * SG)/(N * SSS - SS * SS)
340 LPRINT
350 R = (N*SSG - SS*SG)/((N*SSS - SS*SS)*(N*SGG - SG*SG))0.5
360 LPRINT " N = ";N ; " A = ";A ; " B = ";B ; " R = ";R
370 LPRINT
380 LPRINT "SOLUBILITY G = A + B*S ;B IS THE SLOPE "
390 LPRINT
400 REM TO CHECK FOR DEVIATIONS FOR EACH PAIR OF G AND S"
410 LPRINT " N      G, CALC      G, ACTUAL  DEV      DEV%"
420 FOR I = 1 TO J
430 RHS(I) = A + B*S(I)
440 D(I) = RHS(I) - G(I)
450 PD(I) = 100*D(I)/G(I)
460 SPD = SPD + ABS(PD(I))
470 APD = SPD/N
480 REM RHS = CALCD G; D = DIFFERENCE ; PD = %DIFF
490 REM SPD = SUM OF ABSOLUTE DEVIATIONS; APD = AVERAGE % DEV
500 LPRINT I, RHS(I) , G(I) , D(I), PD(I)
510 NEXT I
520 LPRINT

```

```

530 LPRINT "N = ";N; " APD = "; APD ; " R = "; R ; " J = ";J
540 LPRINT
550 REM BASIS IS 1000 mL OF SOLVENT SOLUTION COLLECTED
560 INPUT "INPUT P = ";P
570 INPUT "INPUT BP = " ; VP
580 INPUT " T = ";T
590 INPUT "INPUT BP = "; BP
595 INPUT "INPUT VP50 = "; VP50
600 REM BP = BAROMETRIC PRESSURE IN ATMOSPHERES
610 INPUT "INPUT SOL50 = "; SOL50
615 REM SOL 50 = SOLUBILITY AT BP AND 50°C IN MOLE FRACTION
620 INPUT "INPUT MSOL = "; MSOL
625 REM MSOL = MOLES SOLUTION IN 1000 mL SOLVENT = 55.33
630 REM FOR WATER
635 INPUT "INPUT NO. = ";NO
640  $PPO_2 = P - VP$ 
645  $A = 32 * SOL50 * MSOL$ 
650  $C = 32 * (BP - VP50) * 1000 * B / (82.05 * 323.15)$ 
655  $SP = A + C$ 
660  $SP1 = SP / PPO_2$ 
665  $XPT = (BP - VP50) * (SOL50 + 1000 * B / (82.05 * 323.15 * MSOL))$ 
670  $XPT1 = XPT / (PPO_2)$ 
675  $H = (PPO_2) / XPT$ 
680 LPRINT
685 LPRINT "P= ";P; "T= "; T; "VP = "; VP; "BP = "; BP;
      " SOL50 = "; SOL50; " MSOL = "; MSOL; "VP50 = "; VP50

```

```
690 LPRINT
700 LPRINT "X AT T,P=";XPT; "XPT1=";XPT1; "H="; H; "NO=";NO
710 LPRINT
720 LPRINT "G/L 50=";A; "G/L AT T=";C; "TOT G/L AT P=";SP;
      "G/L AT 1 = "; SP1
730 LPRINT "END OF PROGRAM"
801 DATA
802 DATA
803 DATA
804 DATA
805 DATA
806 DATA
807 DATA
808 DATA
809 DATA
810 DATA
811 DATA
812 DATA
813 DATA
```