

**The Solubilities of Oxygen in Sulphuric Acid
Solutions Containing Cupric and/or Nickel
Sulphate at Atmospheric and High Pressures**

by

Hanning Li

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



Hanning Li, Ottawa, Canada, 1994



National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file *Votre référence*

Our file *Notre référence*

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-15641-9

Canada



UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

ABSTRACT

The solubilities of oxygen in aqueous solutions, containing sulphuric acid and copper or nickel sulphate, play an important role in a hydrometallurgical process for the recovery of copper called "pressure leaching".

The experimental solutions were prepared as aqueous solutions containing 150 g/l of sulphuric acid and/or cupric cations of 30 g/l or 45 g/l. Another solution was the acid solution containing 150 g/l of sulphuric acid, 45 g/l of cupric ions and 15 g/l of nickel ions. Finally, yet another solution was the acid solution containing 200 g/l of sulphuric acid and 45 g/l of cupric ions. The solubilities of oxygen in aqueous acid-salt solutions were determined at atmospheric and high pressures. At temperatures from 298.15 K to 353.15 K for pressure of 101.3 kPa, the solubilities were measured in an absorption column. At an oxygen partial pressure of 0.5 MPa, the solubilities were measured by means of a two-step method. The solutions were saturated with oxygen at the temperatures of 373.15 K and 413.15 K at the oxygen partial pressure of 0.5 MPa. The oxygen was then desorbed at atmospheric pressure and 313.15 K. Densities and vapour pressures of solutions were also measured at temperatures from 298.15 K to 413.15 K for the determination of oxygen solubilities.

The results showed that the logarithm of oxygen solubilities in aqueous acid-salt solution is linearly related to molar concentration of bivalent cations and densities of acid-salt solutions. A simple model is then suggested to predict oxygen solubilities in the acid-salt solutions. This model has some advantages, compared with the models proposed by Setschenow and by Krevelen and Hofijser. The effects of temperature and pressure on oxygen solubility are also discussed. In the solutions studied, the oxygen solubilities as a function of temperature follow a similar pattern to that in water. For different pressures, Henry's law is obeyed in the range of this research (≤ 5 atm).

ACKNOWLEDGEMENT

The completion of this work represents a productive and effective contribution of others, whose efforts and talents are reflected in the final result. I would like to express my gratitude and appreciation to my supervisor, Dr. W. Hayduk. His guidance, constructive criticism, suggestion and advice made this challenging work. I have learned a great deal from him and I wish to thank him for his efforts.

I extend a sincere word of thanks to the Machine Shop staff for their technical assistance in the construction and maintenance of the equipment. I wish to express my gratitude to the professors, staff and fellow students for making the Department of Chemical Engineering a conducive environment for learning.

I wish also to thank my father and mother. Their efforts and advice which have contributed significantly to my academic achievement, will remain to be my guidance forever. This work is dedicated to them.

NOMENCLATURE

A	Cross sectional area, m^2
B	Secondary virial coefficient
C	Mole concentration, $kmol/m^3$ or mol/l
C^0	Mole concentration in "standard state", $kmol/m^3$ or mol/l
C_i	Electrolyte concentration, $kmol/m^3$ or mol/l
I	Ion strength
K	Henry's law constant, N/m^2
L	Length of the column of solution or solvent, m
P	Total pressure, Pa
R	Gas constant
S	Gas solubility, $kmol/m^3$ or mol/l
S^0	Gas solubility in "standard state", $kmol/m^3$ or mol/l
T	Temperature, K
V	Gas volume, m^3
Z	Ion charge
a	Proportionality constant in equation 29
f	Fugacity, Pa
h	Contribution in equation 10
k_s	Solute-solute gas interaction parameter

k_s	Salt effect parameter in eq 6
k_{scs}	Setschenow salt effect parameter
n	Molar number
p	Partial pressure, Pa
p^0	Vapour pressure, Pa
r	Expansion factor of glass tube
v_i	Partial molar volume of dissolved gas
x	Mole fraction
z	Compression factor
α	Activity, kmol/m ³ or mol/l
β	Calibration constant
γ	Activity coefficient
ρ	Solution or solvent density, kg/m ³
τ	Vibrating frequency reading in the density meter

Subscript

B	Dissolved gas
G	Gas
M	Methanol
T	Operating temperature
W	Water

t Total electrolyte

i Ions

Others

salt Copper sulphate or nickel sulphate

acid Sulphuric acid

u/v/w sulphuric acid in g/l/copper in g/l/nickel in g/l

CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENT	iv
NOMENCLATURE	v
LIST OF FIGURES AND TABLE	xii
1 INTRODUCTION	
1-1 Equipment for the Measurement of Gas Solubility	2
1-1-1 Gas-Bubbler Method	2
1-1-2 Volumetric Methods	4
1-1-3 Thin Film Methods	5
1-1-4 Method for Measurement of Gas Solubility at High Pressure	5
1-1-5 The Methods Used in This Research	6
1-2 The Prediction of Gas Solubilities in Aqueous Acid and/or Salt Solution	7
1-3 Review of Experimental Data for the Solubility of Oxygen in Sulphuric Acid and/or Salt Solution	8
1-4 Scope of the Research	10

2	THEORETICAL ASPECTS	
2-1	Vapour Pressure of Volatile Solute and Henry's Law	11
2-2	Gas Solubility in Electrolyte Solutions	12
2-2-1	Setschenow Salt Effect Parameter	13
2-2-2	The Effect of Ionic Strength	15
3	METHODOLOGY FOR PREPARATION OF SOLUTIONS, MEASURING DENSITIES, VAPOUR PRESSURE AND OXYGEN SOLUBILITIES	
3-1	Preparation of Solutions	17
3-2	The measurement of the Solution Densities at 25°C	18
3-2-1	Measurements of Densities Using A Densimeter	18
3-2-2	The Calibration of the Densimeter Using Water and Methanol	19
3-3	The Measurement of Liquid Densities at Higher Temperatures Using Dilatometer Tubes	21
3-3-1	Dilatometer Tubes	21
3-3-2	Calculation of the Density at High Temperatures	24
3-4	The Measurement of Oxygen Solubilities in the Aqueous Electrolyte Solutions at Low Temperatures and Pressures	26
3-4-1	Degassing Procedure	26

3-4-2	Absorption Procedure for Oxygen Solubility	
	Determinations	28
3-5	The Measurement of Oxygen Solubility in Water and Aqueous Electrolyte Solutions at Elevated Temperatures and Pressures	32
3-5-1	Absorption Procedure at High Temperatures and Pressures	32
3-5-2	Desorption Procedure at Lower Temperature and Pressure	36
3-6	The Principle of Calculation for the Solubility Results	38
3-6-1	The Calculation at Lower Temperatures and Pressures	38
3-6-2	The Calculation at higher Temperatures and Pressures	41
3-7	The Measurement of Vapour Pressure of the Aqueous Electrolyte Solutions	43
3-7-1	Description of Equipment for the Measurement of Vapour Pressure	43
3-7-2	Procedure	45
3-7-3	Calibration of Transducer for Vapour Pressure	46

4 RESULTS AND DISCUSSION

4-1	The Solubilities at Atmospheric Pressure and Temperatures from 298.15 K to 353.15 K	48
4-1-1	The Effects of Cations Cu^{++} and Ni^{++} on the Oxygen Solubility in Aqueous Sulphuric Acid Solution	50
4-1-2	Densities of Aqueous Electrolyte Solutions	54
4-1-3	The Relation between Solution Density and Oxygen Solubilities in Aqueous Acid Solutions Containing Copper and/or Nickel Ions	58
4-1-4	A New Simple Model to Predict the Oxygen Solubility in Aqueous Acid-Salt Solution	61
4-1-5	The Comparison of the Models	63
4-2	The Oxygen Solubilities in Water and Aqueous Acid-Salt Solutions at Elevated Temperatures and a Pressure of 0.5 MPa	65
4-3	The Effects of Temperature on Oxygen Solubility in Water and Aqueous Acid-Salt Solution	68
4-4	General Discussion	69
	CONCLUSIONS	71
	REFERENCES	73

APPENDIX A	76
APPENDIX B	79
APPENDIX C	82
APPENDIX D	83
APPENDIX E	84
APPENDIX F	87
APPENDIX G	89

LIST OF FIGURES AND TABLE

Figure 1	Experimental Apparatus	3
Figure 2	Dilatometer Apparatus with Sealing Connection Between the SS Tubing and Glass Dilatometer	23
Figure 3	Solubility Equipment for Atmospheric Pressure	31
Figure 4	Solubility Equipment for High Pressure	35
Figure 5	Equipment for the Measurement of Vapour Pressure of Aqueous Electrolyte Solution	44
Figure 6	Mole Fraction Oxygen Solubilities in Water and Aqueous Acid-Salt Solutions at Atmospheric Pressure	49
Figure 7	Oxygen Solubility versus Concentration of Dissolved Salts	52
Figure 8	Logarithm of Oxygen Solubility versus Concentration of Dissolved Salts	53

Figure 9	Densities of the Aqueous Acid-Salt Solutions versus Temperature	56
Figure 10	Solution Density versus Salt Concentration in the Acid-Salt Solutions	57
Figure 11	The Logarithm of Oxygen Solubility in the Acid-Salt Solution Density	60
Figure 12	Mole Fraction Oxygen Solubilities in Water and Aqueous Acid-Salt Solutions at Atmospheric Pressure	69
Figure 13	Plot of the Volumes of Gas versus Volumes of Solution for a Solution Containing 150 g/L Acid, 30 g/L Copper Ions	95
Table 1	The Ratio of Oxygen Solubilities in the Acid Solution to that in Water	62

1 INTRODUCTION

This thesis concerns the measurements of solubilities of oxygen in a solution containing sulphuric acid and bivalent cations of copper and/or nickel. The experimental results are useful in the hydrometallurgical process for the recovery of copper during the electrorefining process. It is necessary that all the copper is oxidized to its highest oxidation state for a high recovery of the purified metal. Oxygen gas is sometimes used as the oxidizing medium.

The gas solubility in a liquid depends on temperature and the partial pressure of the gas. The solubility measurements require the determination of a temperature, a pressure and the corresponding composition of the liquid phase (Battino and Clever, 1966).

The temperature is an important parameter in the measurement of gas solubility. Errors in the temperature will cause the errors in gas solubility. Therefore, accurately controlled temperature is an important step in the measurement of solubility. Normally, the temperature is controlled to $\pm 0.1^\circ\text{C}$.

The vapour phase in a gas absorption experiment contains at least two components: the tested gas and solvent vapour. The total pressure of the vapour

phase can usually be measured accurately. The partial pressure of the tested gas can be estimated based on the total pressure and vapour pressure of solvent.

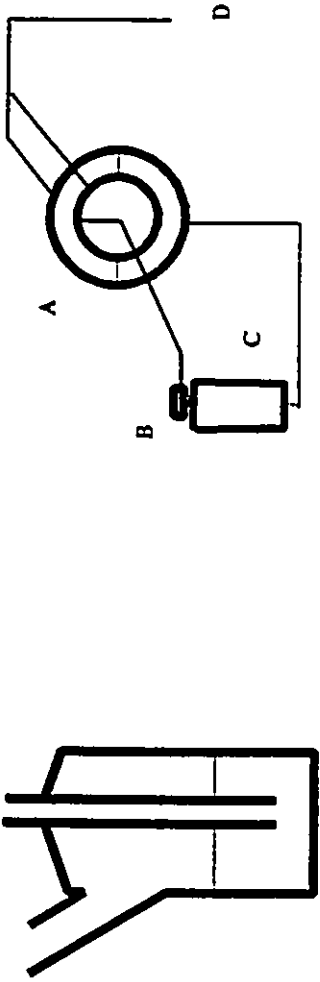
Therefore, gas solubility at a tested partial pressure and a known temperature can be obtained from experimental data of the volume of absorbed gas in a unit volume of liquid. Then, mole fraction solubility can be obtained by using the known gas and liquid mole volumes.

Based on these basic requirements, many authors have utilized different ways to measure gas solubility at any temperature and pressure. The experimental equipment for the measurement of gas solubility at atmospheric pressure and high pressure will be described as follows:

1-1 Equipment for the Measurements of Gas Solubility

1-1-1 Gas-Bubbler Method

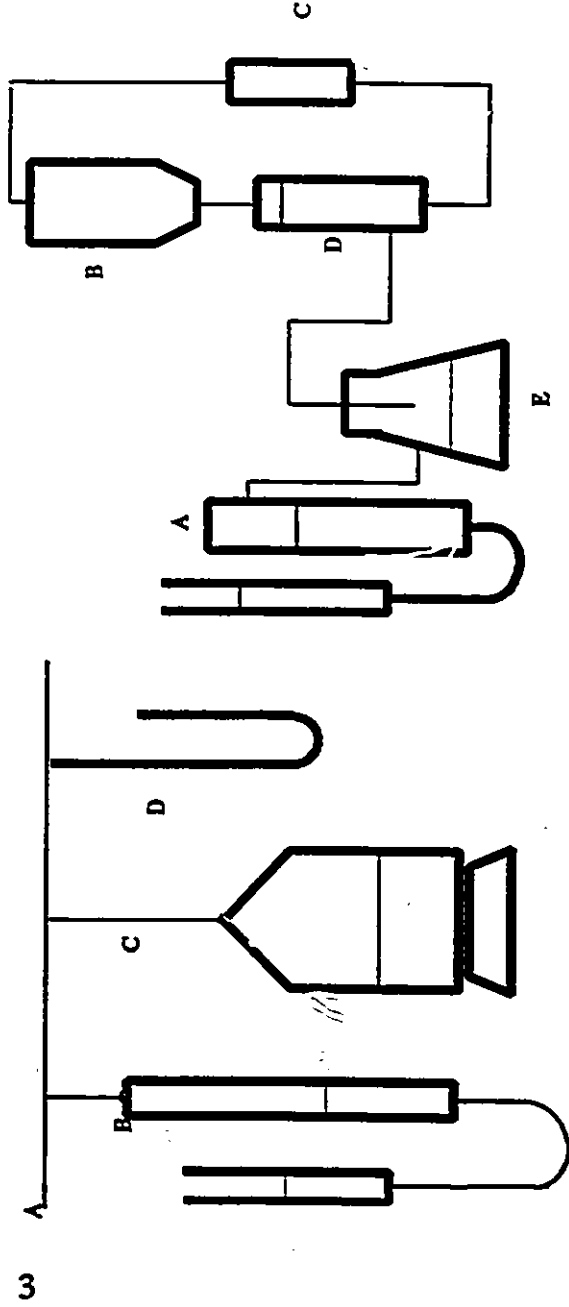
A simple gas-bubbler apparatus consists of an absorption vessel with an inlet tube to pass gas below the surface of a solvent, and an outlet tube, as shown in Figure 1-a (Gerrard, 1976). The vessel and its contents are held in a constant temperature bath. The gas is bubbled through the liquid until no further gas is absorbed. The total pressure above the liquid is normally equal to atmospheric pressure and is the sum of the partial pressure of the gas and the vapour pressure



(a)

(a) Gas-Bubbler

(b) Volumetric Methods
 A. gas source
 B. gas burette
 C. absorption vessel
 D. manometer



(b)

(c) Thin Film
 A. absorption vessel
 B. liquid source
 C. gas source

(d) Equipment for High Pressure
 A. gas burette
 B. vapour reservoir
 C. magnetic pump
 D. liquid reservoir
 E. sample vessel

(d)

Figure 1 Experimental Apparatus

of the solvent. The quantity of gas absorbed is found by chemical analysis or weighing the vessel and its contents.

1-1-2 Volumetric Methods

In this type of apparatus, a measured volume of gas at a constant pressure and temperature comes into contact with a measured quantity of solvent with appropriate agitation to ensure that equilibrium is established between gas and liquid phases. The volumes of the gas phase before and after absorption are measured at the same pressure, usually atmospheric pressure. The amount of absorbed gas is measured from the difference between the initial and final volumes of gas.

A typical apparatus of this type was reviewed by Clever and Battino (1975). As shown in Figure 1-b, this apparatus consists of a calibrated gas burette, B, and magnetically stirred absorption vessel, C, connected by capillary tubing to a vacuum line, A, and a source of gas. The temperature of the gas burette and the absorption vessel must be controlled. Gas under test is introduced over mercury into the gas burette from a reservoir of gas. The volume of gas in the burette is measured at atmospheric pressure. The space above the solvent and in the capillary tubes are evacuated. Gas from the burette is then allowed to come into contact with the solvent, which is magnetically stirred until equilibrium is reached. The pressure during the absorption is controlled by the difference in mercury

levels in the two arms of the gas burette and is measured by manometer D. When equilibrium is reached, the volume of gas in the gas burette is measured at atmospheric pressure.

1-1-3 Thin Film Methods

In this type of measurement of gas solubility, a thin film of liquid comes into contact with the gas. As shown in Figure 1-c, the equipment consists of an equilibrator which consists of two concentric glass spheres with inner and outer volumes of about 1 dm³ and 2 dm³, respectively (Benson and Krause, 1979). Solvent is pumped from the liquid sample bulb into the space between the inner and outer spheres. Then the solvent falls as a thin film and circulates back to the sample bulb. The gas fills the inner sphere and the part of the space between the two spheres not occupied by liquid. Equilibrium between gas and liquid phases is established at the surface of the thin film of liquid.

After an appropriate time, a volume of the liquid phase is sealed off in a liquid phase sample bulb and analyzed. Equilibrium is reached when there is no further change in composition of the phases with circulation of liquid.

1-1-4 Method for Measurement of Gas Solubility at High Pressure

The apparatus for such studies is usually constructed largely of steel. There is often provision to withdraw samples of the liquid phase and the gas phase while

the system is under pressure.

Lee and Mather (Fogg and Gerrard, 1990) constructed an apparatus for measurement of gas solubility at high pressure in water, as shown in Figure 1-d. The cell consists of a high pressure liquid level gauge of capacity 200 cm³ (D) mounted below a vapour reservoir of capacity 250 cm³ (B). The cell is charged with about 100 cm³ of water. The gas at the required pressure is circulated through the cell by a magnetic pump (C). Pressure and temperature are measured. The cell and pump are housed in an air-bath.

Small samples of the liquid phase are withdrawn through a valve into a sampling vessel at atmospheric pressure (E). Gas evolved from the liquid in this vessel is collected in a gas burette (A). The residual liquid in the vessel, after evolution of this gas, is analyzed by gas chromatography. There is also a procedure for withdrawing samples of the gas phase from the cell directly into a chromatograph.

1-1-5 The Methods Used in this Research

In this research, the solubility at atmospheric pressure was measured in a way similar to the thin film method as developed by Morrison and Billett (1948). The degassed solvent is introduced into a spiral tube and the gas is confined in the tube, as shown in Chapter 3. While the solvent flows slowly at a constant rate through the tube, the gas is absorbed in the solvent. The amount of residual gas

is observed in a burette, which is maintained at atmospheric pressure.

The solubility at high pressure was conducted in two stages, the first equilibration at high pressure in an absorption cell and the next desorption in the same column as that used in measurement of gas solubility at atmospheric pressure. The solvent, saturated with gas is introduced into the spiral tube, where the gas is released from solvent into the tube, as shown in Chapter 3. The tube is connected to a burette, in which the amount of released gas is observed. Combined with the solubility which is measured at the temperature of 313.15 K at atmospheric pressure, the solubility at high pressure is obtained.

1-2 The Predictions of Gas Solubilities in Aqueous Acid and/or Salt Solutions

Gas solubilities in water and aqueous salt solutions have been measured by a number of workers (Morrison and Billett, 1948; Ying Hu, Yingnian and Prausnitz, 1987; Kimweri, 1990). When a salt is added to water, the gas solubility is reduced from its solubility in pure water. This is called 'salt out'. To explain this phenomenon, a number of authors have suggested different models to predict the effect of concentration of salts on gas solubility.

One of them is the well-known empirical Setschenow equation (Battino, 1981). In this model, the logarithm of relative gas solubility in water and salt solution is proportional to the concentration of the salt. The proportionality

constant, called as the Setschenow salt-effect parameter, depends on the temperature and the concentration of salts.

Another model is the Ionic Strength Model (Danckwerts, 1970). In this model, the logarithm of relative gas solubility is proportional to the ionic strength. The proportionality constant is a contribution, which depends on the temperature and the type of ions.

Based on the experimental results in this research, a simple model is suggested to predict the oxygen solubility. In this model, the logarithm of relative oxygen solubility is proportional to the density difference between acid and salt. The proportionality constant is independent of the temperature.

1-3 Review of Experimental Data for the Solubility of Oxygen in Sulphuric Acid and/or Salt Solution

Very few workers have measured the solubility of oxygen in sulphuric acid solutions. In the review of oxygen solubility data, in an IUPAC publication by Battino (1981), there were only six recorded sets of measurements for the gas solubility in aqueous sulphuric acid solutions. All the results indicate the following trends:

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

of the acid. As expected, the gas solubility increases with the increase in partial pressure of oxygen at a constant temperature as expressed by Henry's law.

Gubbins and Walker (Battino and Clever, 1966) measured the solubility of oxygen in sulphuric acid solutions at higher concentrations of the acid. The results indicated that oxygen solubility decreases to a minimum at about 80% by mass H_2SO_4 and then increases sharply as 100% by mass H_2SO_4 is approached.

Measurements made by Brun et al. (1965), at five temperatures between 323 K and 523 K and for the concentrations of 0.5, 1.0 and 1.5 mol/L sulphuric acid solutions, show a minimum solubility at the temperature of about 373 K.

Kleva (Kimweri, 1990) measured the solubility of oxygen in aqueous sulphuric acid solution containing salts. He measured the solubilities at oxygen partial pressures of 0.25 MPa and 1.0 MPa at six temperatures between 323 K and 473 K. Concentration of the solutions was 0.0125 mol/L sulphuric acid saturated with either nickel, copper or cobalt sulphide. The sulphuric acid-metal sulphide concentration lowered the oxygen solubility to less than 50% its solubility in water. The variation of oxygen solubility with temperature and partial pressure of oxygen followed the same trend as that for the aqueous sulphuric acid solution.

1-4 Scope of the Research

This research is aimed at determining the oxygen solubility in an aqueous sulphuric acid solution and three other solutions containing different amounts of the dissolved salts, copper and/or nickel sulphate, at temperatures between 298.15 K and 353.15 K for a pressure of 0.101 MPa. The measurements of solubilities were also conducted for the temperatures of 373.15 K and 413.15 K and the oxygen partial pressure of 0.5 MPa.

For the above solutions, the densities and vapour pressures were also determined at each temperature for the solubility calculation.

2. THEORETICAL ASPECTS

2-1 Vapour Pressure of a Volatile Solute and Henry's Law

For dilute solutions, the gas solubility 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 (Levine, I.N., 1983):

$$p_B = K_B x_B \quad (1)$$

In the above equation, K_B is the Henry's law constant which 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 do 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 actual experimental pressure

to a partial pressure of one atmosphere (as described in the chapter of Methodology), if the mole fraction of the gas is small.

At higher pressures, the Henry's law constant is also a function of pressure (Danckwerts, 1970; Chengfang, Zhang, 1985) which is expressed by:

$$\frac{d (\ln K_B)}{d P} = \frac{d \ln\left(\frac{x_B}{P_B}\right)}{d P} = \frac{v_B}{R T} \quad (2)$$

Equation (2) relates the partial molar volume of dissolved gas to the Henry's law constant.

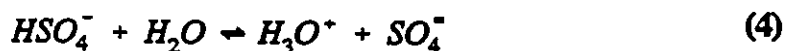
2-2 Gas Solubilities in Electrolyte Solution

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; 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 and then dissociate to some extent to yield ions. For example, sulphuric

acid reacts with water according to:



In a dilute solution, a further reaction occurs:



In electrolyte solutions, both dissociation and association of ions are always taking place. These ions, in the form of free particles, affect gas solubility in the electrolyte solution. As a result, these charged particles reduce gas solubility in the solution. Some authors suggested some methods or models for predicting the effect of ions (or salts) on gas solubility. Two models (the Setschenow salt effect parameter, and the ionic strength effect) are introduced for this purpose.

2-2-1 Setschenow Salt Effect Parameter

Studies concerning the effect of dissolved salts on gas solubility are well presented by Battino and Clever (1966) and also summarized in an IUPAC publication (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 a negligible chemical interaction between solute species, the logarithm of the dissolved gas activity

coefficient can be represented as:

$$\log \gamma_B = k_s C_s + k_B C_B \quad (5)$$

In the above expression, k_s is the salt effect parameter, k_B is the solute-solute gas interaction parameter (Kimweri, 1990).

It is considered that the dissolved gas activity in the pure solvent is same as that in the solution. That is,

$$a_B = \gamma_B S_B = \gamma_B^0 S_B^0 \quad (6)$$

In the above equations, S_B and S_B^0 are the gas solubilities in the solution, and in the pure solvent. Also, γ_B and γ_B^0 are their corresponding activity coefficients. Therefore, the following equation results:

$$\log \frac{\gamma_B}{\gamma_B^0} = \log \frac{S_B^0}{S_B} = k_s C_s + k_B (C_B - C_B^0) \quad (7)$$

If the gas solubilities are low, the term with k_B can be neglected, thus:

$$\log \frac{\gamma_B}{\gamma_B^0} = \log \frac{S_B^0}{S_B} = k_s C_s \quad (8)$$

From the above equation, the Setschenow salt effect parameter, k_{SCA} , is

defined as follows:

$$k_{SCA} = \frac{1}{C_t} \log\left(\frac{S_B^O}{S_B}\right) \quad (9)$$

In the above equation, C_t is the total electrolyte concentration.

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 gas solubility, whereas salting in implies increasing its solubility.

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

2-2-2 The Effect of Ionic Strength

Based on the Setschenow salt effect parameter, Krevelen and Hofstijzer (Danckwerts, 1970) proposed a method to estimate the solubility in electrolyte solutions. In this method, the Henry's law constant in the solution is related to that in water at the same temperature as shown in the following expression:

$$\log\left(\frac{K_B}{K_B^O}\right) = \log\left(\frac{S_B^O}{S_B}\right) = h_1 I_1 + h_2 I_2 + \quad (10)$$

In the above equation, I is the ionic strength of the solution defined by:

$$I_i = \frac{1}{2} \sum C_i (Z_+^2 + Z_-^2) \quad (11)$$

The effects of the different species on gas solubility in an electrolyte solution are expressed by

$$h = h_+ + h_- + h_G \quad (12)$$

In the above expression, h_+ , h_- , h_G are the contributions or effects on gas solubility by the positive ions, of negative ions, as well as the dissolved gas in solution. Thus, the total effect of the gas solubility is simply the sum of the effects of the dissolved molecular or ionic species.

Until now, the Setschenow Salt Effect Parameter has been most useful in the prediction of gas solubility in salt solutions. However, it is inconvenient, because each parameter corresponds to a given temperature and composition of solution. Compared with the Setschenow Salt Effect Parameter, the method suggested by Crevenlen is more convenience, because the parameters (h_+ , h_- , h_G) in the model are independent of the composition of aqueous salt solution (details are described in chapter 4).

3. METHODOLOGY FOR PREPARATION OF SOLUTIONS, MEASURING DENSITIES, VAPOUR PRESSURE, AND OXYGEN SOLUBILITIES

In this chapter, the experimental equipment, instruments and procedures which were used in this research are described. The experimental equipment was used in the determination of the densities and vapour pressures of the aqueous sulphuric acid-metallic salt solutions, and oxygen solubilities in the solutions. There is also a section in this chapter describing the calculation performed on the experimental data.

3-1 Preparation of Solutions

The aqueous electrolyte solutions were prepared using 98.0% sulphuric acid (H_2SO_4), 98.0% hydrated cupric sulphate ($Cu_2SO_4 \cdot 5H_2O$), and 98.0% hydrated nickel sulphate ($Ni_2SO_4 \cdot 6H_2O$), all from BDH Inc.. All these chemicals were of the analytical grade.

The volume of the concentrated sulphuric acid was determined using volumetric flasks and burettes. The weight of cupric sulphate or nickel sulphate was determined using a balance.

The prepared sulphuric acid was partly diluted in the 1-litre volumetric flask using distilled water. The prepared salts were then added into the solution. Distilled water was added into the volumetric flask until it was filled to 1-litre.

3-2 The Measurement of Solution Densities

The densities of the solutions were measured at temperatures from 298.15 K to 413.15 K in this research. The densities were determined in two different ways depending on the temperature. A highly accurate digital densimeter was used for the determination of the densities of solutions at a temperature of 298.15 K; whereas a dilatometer was used in the determination of solution densities at temperatures from 313.15 K to 413.15 K. The solution densities could not be determined by the densimeter at high temperatures (such as above 373.15 K), because this expensive equipment would be corroded at high temperature.

3-2-1 Measurements of Densities Using a Densimeter

At a temperature of 298.15 K, an Anton Parr, vibrating-reed digital density meter was used to measure the solution densities. The advantage of this equipment was its high accuracy. When the temperature was kept constant, duplicate results of density could be obtained to 0.1 kg/m³.

The 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 unit was the DMA 600, which was a frequency counter and a digital display unit. From the digital display unit, the vibrating frequency of the reed was obtained for the calculation of the solution density.

In each experiment, a sample of water or aqueous electrolyte solution was injected into the density meter using a plastic syringe which had a capacity of 2 mL. The solution was then exposed to a constant temperature of 298.15 K in the U-tube which was surrounded by a water jacket. After a few minutes, the vibrating frequency reading on the densitometer remained essentially constant with time. To obtain the experimental average result, several readings of the vibrating frequency were taken for each solution. The average value of each solution was then used in the calculation of the solution density.

3-2-2 The Calibration of the Densitometer Using Water and Methanol

The experimental results from the densitometer were the data for vibrating frequencies. The theory for density measurements suggests that the density of the liquid in the densitometer is proportional to the square of the vibrating frequency of the vibrating reed. The proportionality constant at 298.15 K is obtained by utilizing the liquids, whose densities are accurately known. In this case, distilled water and methanol were chosen. Therefore, an empirical equation was applied to relate the vibrating frequency to the density of the solutions. The equation is

as follow:

$$\rho_W - \rho_M = \frac{1}{\beta} (\tau_W^2 - \tau_M^2) \quad (13)$$

In the above equation, ρ_W and ρ_M are the densities of the two reference liquids. For this purpose, water (W) and methanol (M) were chosen as the reference liquids. The calibration constant, β , was obtained from the known densities and vibrating frequencies as follows:

$$\beta = \frac{\tau_W^2 - \tau_M^2}{\rho_W - \rho_M} \quad (14)$$

The equation written in terms of the vibrating frequency is

$$\rho = 3.394802\tau^2 - 1.057916 \quad (15)$$

From the experimental data of vibrating frequency in each solution, the solution densities were obtained using Equation 15. The experimental data and results for the densities of solutions at 298.15 K are listed in Appendix A-1.

3-3 The Measurement of Liquid Densities at Higher Temperature using Dilatometer Tubes

Unlike the case at 298.15 K, the densities of solutions at higher temperature were measured by using dilatometer tubes, because the expensive densimeter would have been damaged by the corrosive solutions at higher temperature.

3-3-1 Dilatometer Tubes

For temperatures between 313.15 K and 413.15 K, the densities of water and the aqueous electrolyte solutions were measured by means of dilatometers. The dilatometers were used to measure the dilation of the solutions as the temperatures were increased. The dilatometers were made of pyrex glass capillary tubing of uniform cross-sectional area having an internal diameter of 0.8 mm. One end of each tube was sealed by glass blowing. The other open end was connected to a pressurizing system.

The solution whose densities was to be measured was charged into the capillary tube by means of a long and flexible plastic tube of the diameter of 0.5 mm, which was also used in filling the dilatometers and preventing the formation of air bubbles. To obtain an accurately measurable degree of dilation of the solution, a minimum length of solution to be charged was considered to be about 0.3 m. Four such dilatometers were constructed to measure the densities of the

solutions. The tubes were connected to a pressurizing system, which consisted of a compressed oxygen cylinder connected to four dilatometer tubes.

The pressurized dilatometer tubes, filled with water or aqueous solutions, were immersed in an oil bath initially maintained at 298.15 K. The temperatures in the oil bath were then increased from 298.15 K to desired temperature, at which the lengths of the columns of solutions were measured.

The dilatometer tubes were pressurized to a total pressure above the vapour pressure of the solutions even for the highest temperature utilized. The purpose of pressurization was to prevent the solutions from boiling, because the solution whose densities were measured would be above the normal boiling point of water.

The initial length of solution inside each capillary tube was recorded at the temperature of 298.15 K. The lengths of the solutions confined in the tubes were accurately measured by using a cathetometer readable to 0.01 mm. White lines were marked on the outside of each capillary tube as reference points to identify the lengths of the solutions in the tubes. To permit immersion of the complete lengths of tubes, the dilatometer tubes were bent to form a 90°-angle, as shown in Figure 2. Thus, the tubes were partly filled allowing a significant expansion of the solutions as the temperature was increased to 413.15 K.

The results were obtained as the actual lengths of the column of solutions inside the tube. The lengths of the measured columns of the solutions were then used to calculate the densities of the solutions by mass balances.

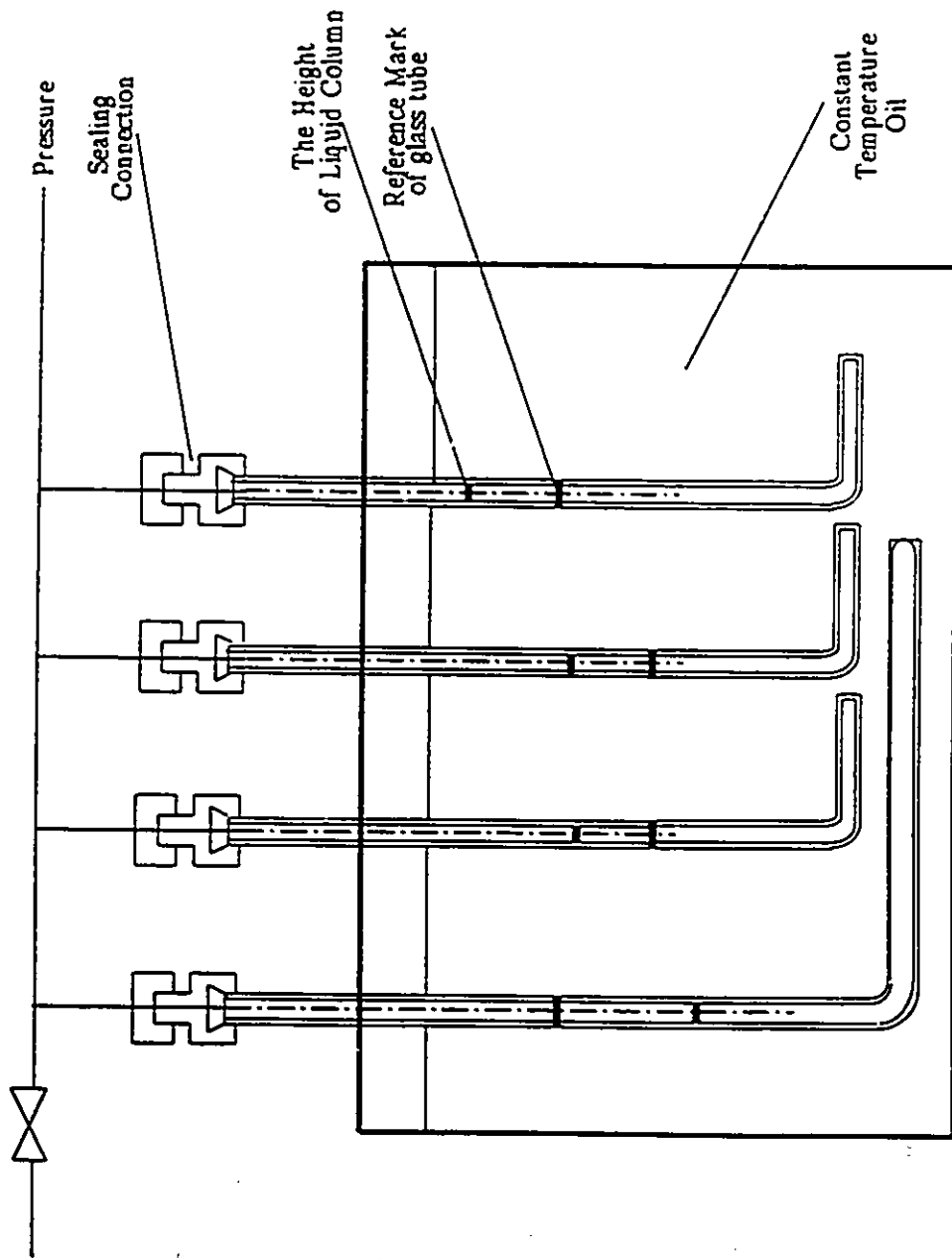


Figure 2 Dilatometer Apparatus with Sealing Connection Between the SS Tubing and Glass Dilatometer

The dilatometers were calibrated by using distilled water. This was necessary because the glass tubes had a small but measurable coefficient of expansion. The purpose of calibrations was to find the small correction factors which would take into account for the effects of the expansion of the tubes on the lengths and cross sectional areas of the columns of the solutions.

3-3-2 Calculation of the Density at High Temperatures

To obtain the densities from the lengths of the columns of the solutions, mass balances were applied. If the loss of water by evaporation is neglected, the mass of the solution is assumed to be same at all temperatures. The mass of solution inside each tube is expressed in the terms of the density of the solution, the cross-sectional area of the capillary tube (A) and the length of the solution inside the tube (L):

$$\rho_{25^{\circ}C} A_{25^{\circ}C} L_{25^{\circ}C} = \rho_T A_T L_T \quad (16)$$

Since the capillary tubes in these experiments are of uniform cross-sectional area, Equation 16 becomes:

$$\rho_{25^{\circ}C} L_{25^{\circ}C} = \rho_T L_T \quad (17)$$

As the temperature is increased, the glass tube will expand, although the

coefficient of expansion of water is considerably larger than that of pyrex glass. The change of the tube length can be accounted for by comparing the length of the tube at the higher temperature with that at the temperature of 298.15 K. A parameter 'r' was applied in Equation 17 to correct the length of the column of the solution in the capillary for expansion of the glass tube:

$$\rho_{25^{\circ}\text{C}} L_{25^{\circ}\text{C}} = \rho_T L_T r \quad (18)$$

By using the solution densities measured at 298.15 K by densimeter and the lengths of the columns of the solutions measured at 298.15 K and at the higher temperatures, the densities at the higher temperatures were calculated using Equation 18. The value of 'r' was determined by comparing the length of the column of the distilled water at the higher temperature with that at a temperature of 298.15 K.

The experimental results of the lengths of the columns of solutions for temperatures from 298.15 K to 413.15 K are listed in Appendix A-2. Appendix A-2 also shows the expansion factors of the glass tube lengths for the same temperatures. For temperatures less than 353.15 K, the expansion factor was found to be negligible, so that they were not listed. The densities based on Equation 18 are represented in Appendix A-3.

3-4 The Measurement of Oxygen Solubilities in the Aqueous Electrolyte Solutions at Low Temperatures and Pressures

In this section, the solubility measurements of oxygen in water and aqueous electrolyte solution are explained for low temperatures and 101.3 kPa pressure. For high temperatures and for pressures greater than 101.3 kPa, the solubility measurement is explained in the next section.

For the measurement of oxygen solubility at atmospheric pressure, a two-step procedure was applied. First, the solution was degassed by means of vacuum. Next, the degassed solution was injected into the absorption system where oxygen was absorbed at atmospheric pressure at constant temperature.

3-4-1 Degassing Procedure

Prior to the measurement of oxygen solubility, any gas present in water or aqueous electrolyte solution was removed, so as to measure only the amount of oxygen absorbed by the deaerated solutions. If any gas (mainly air) was present in the solutions during the solubility measurement, it would interfere with gas solubility results.

A degassing system served this purpose. It consisted essentially of a reservoir, a solvent degassing and storage column, and a vacuum pump. The column, filled with beads, was used for degassing the solutions. The column and

the beads inside the column were made of glass. Because of the low solubility of oxygen in water and in aqueous solutions, the volume of solvent solution required for absorption was approximately 400 ml. To supply this amount of solvent solution, the solvent degassing column was constructed of 1.5 m in length and 0.04 m in diameter. The beads, having a diameter of 1 mm, were used as a packing for this column to provide the necessary interfacial area so as to improve degassing.

A reservoir was situated above the top of the bead column for an initial stage of deaeration. A magnetic stirring bar inside the reservoir was used to improve degassing. A vacuum pump served to provide the vacuum for the reservoir and the column. Having been partially degassed in the reservoir, the solution was allowed to flow out from the reservoir and into the evacuated bead column by gravity. When degassed solution filled the column, air was allowed to flow to the top of the column and the vacuum pump was turned off. A diagram of this equipment is shown in Figure 3.

The degassing procedure is now described in a more detail: The prepared solution was put into the reservoir and evacuated there until the solution began to boil. A stirring bar was used to accelerate the degassing process. This process was continued for about one hour until very few bubbles came out of the solution. Next, the cock was opened slightly so that the solution inside the reservoir was allowed to dribble slowly into the packed column.

It was considered that the solution needed further degassing in the packed column to remove any residual gas. When the solution was filled in the packed column, the top of the column was opened to atmosphere. At this pressure, the solution could be pumped into the top of absorption column when required. The solution inside the packed column remained totally deaerated, because the air could not diffuse quickly through the top section of the degassed solution in the packed column.

The degassed solution from the bottom of the bead column was pumped at a constant rate into the top of the absorption column by means of a mini pump. At the absorption column, the absorption procedure will be fulfilled.

3-4-2 Absorption Procedure for Oxygen Solubility Determinations

In the absorption procedure, oxygen was absorbed by the degassed aqueous solution. The rate of dissolution of oxygen in the aqueous solution was measured. This process was realized by observing the residual oxygen volume in the gas burette of the solubility apparatus (Hayduk et al., 1972, 1988). The absorption apparatus was of glass. It consisted of a spiral coil through which the solution flowed as a thin film, so that the solution absorbed the oxygen inside the spiral coil, as shown in Figure 3. At the top, the coil was connected to gas burette initially filled with oxygen. At the bottom, it was connected to a small U-tube manometer through which the saturated solution flowed out. The small U-tube

manometer acted as a seal, confining the gas in the spiral coil between the U-tube and the mercury located at the bottom in the gas burette. The manometer also served as a very sensitive pressure indicator for comparing the internal pressure inside the spiral coil with the atmospheric pressure.

To maintain a constant pressure inside the burette and the spiral coil, a mercury lift machine driven by a variable speed motor was used to control the lift-speed as required in the experiment for constant pressure. At the beginning of absorption, gas burette and spiral coil were flushed with pure oxygen and solvent was pumped through the absorption spiral simultaneously.

In the absorption apparatus, including the burette and the spiral coil, temperature control was achieved by circulating water at the desired temperature through a water jacket surrounding the apparatus. The water was heated in a water bath (TAMSON TCV 70) and then pumped into water jacket. Using this method, the apparatus could be maintained at a constant temperature. However, at higher temperatures (such as 353.15 K), the apparatus appeared to have a high heat loss which caused a drop in temperature of about 2.5 K between the water inlet and water outlet from the absorption apparatus. To reduce the heat loss, a transparent plastic sheet was used as an insulator around the whole absorption column. In addition, the tubes which circulated the constant temperature water were covered by fibre insulation. Further, a higher flow rate of the water was also helpful in reducing the temperature difference to ± 0.2 K at the operating

temperature of 353.15 K.

Gas solubility was determined based on the constant solution flow rate and the absorption rate of oxygen. The solution flow rate was obtained by observing the volume of solution flowing from the column and accumulated in a graduated cylinder; at the same time, the absorption rate of oxygen was obtained by reading the level of mercury in the gas burette and observing the change in volume of oxygen at constant temperature and pressure. For each solubility experiment, more than ten data of solution volume and oxygen volume were obtained. One experiment took from 60 to 90 minutes to complete. The obtained data were then used in the calculation of solubility.

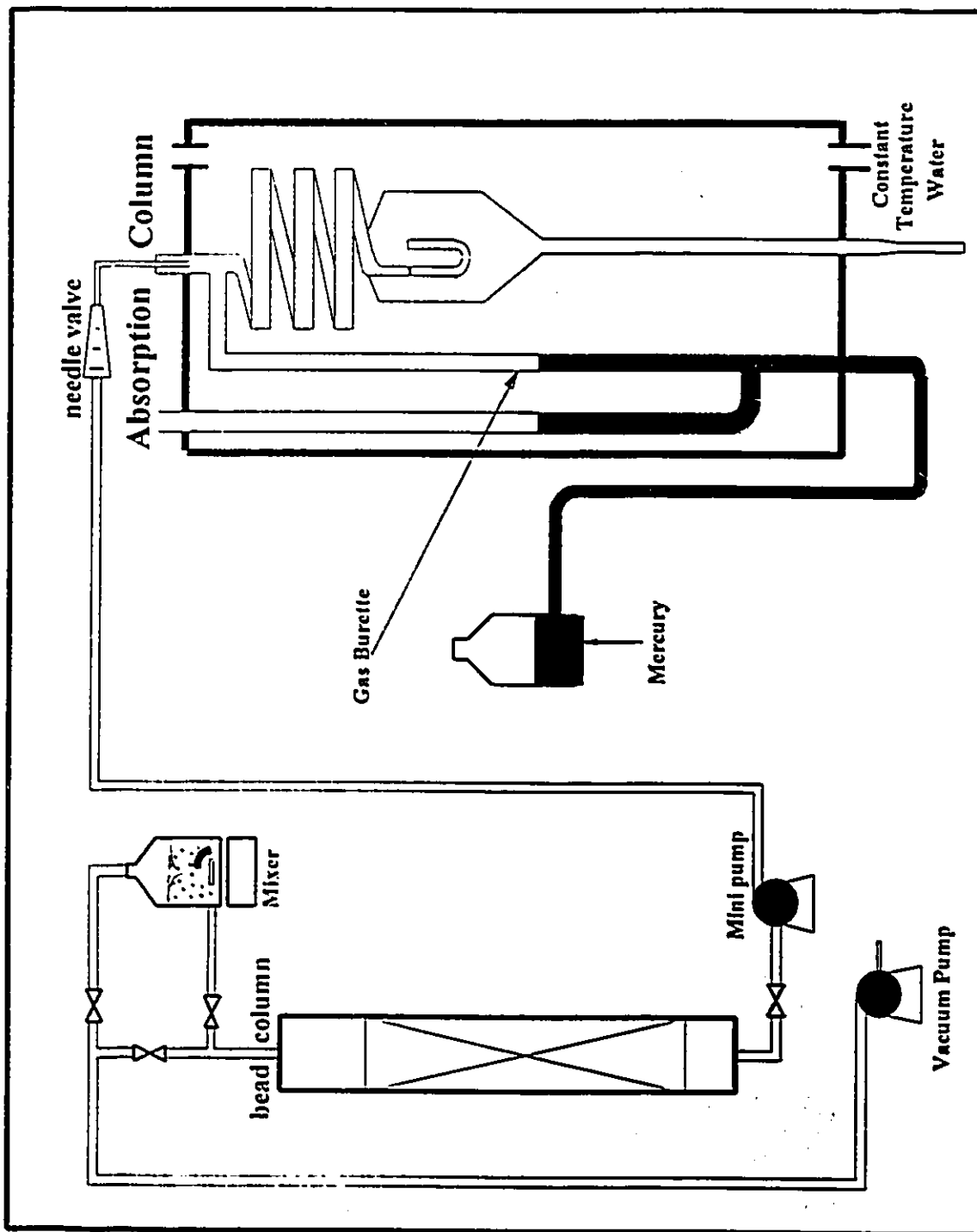


Figure 3 Solubility Equipment for Atmospheric Pressure

3-5 The Measurement of Oxygen Solubility in water and Aqueous Electrolyte Solutions at Elevated Temperatures and Pressures

In determining the solubilities at higher temperatures and pressures, a two-step method was used which was different from that at lower temperatures. First, oxygen was absorbed at constant temperature and pressure in a high pressure equilibration cell, which served first as a deaeration vessel and then used for equilibration at a partial pressure of oxygen of about 0.5 MPa; Next, the solution, saturated with oxygen, was directed to a glass desorption apparatus, which was operated at atmospheric pressure and a temperature of 313.15 K. The solubility was then measured based on the volume of oxygen released at the lower pressure for a defined volume of the solution. The desorption apparatus in this case was the same as that used for absorption at low pressure. In this case, however, the rate of oxygen released was measured in the gas burette when the solvent was allowed to flow into the apparatus at constant rate.

3-5-1 Absorption Procedure at Higher Temperatures and Pressures

The high pressure absorption apparatus consisted of a stainless steel (SS 316) pressure vessel with a solution capacity of 600 ml (see Figure 4). The vessel was equipped with a pyrex glass insert to prevent direct contact between the

sulphuric acid solution and stainless steel preventing the corrosion of the stainless steel which could result by contact with sulphuric acid at high temperatures. The glass vessel was also easier to clean than a stainless steel one. The vessel was provided with a magnetic stirring bar. The magnetic stirrer bar used was a conventional one consisting of a small 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 1/8-inch stainless steel (SS 316) tube was immersed in an 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 products of corrosion are swept away by the flow conditions. This tube was also used in discharging the solution after the equilibrium was reached and for conveying it to the desorption apparatus.

The sealed high pressure absorption vessel was charged with the solution. The closed vessel was then immersed in the oil bath at a lower temperature of 298.15 K. Degassing was achieved by applying a vacuum. During the degassing procedure, the solution was agitated by using the magnetic stirrer. The purpose of stirring was to continuously expose new liquid surfaces to vacuum so as to

improve the degassing.

After degassing, the absorption vessel was pressurized with oxygen to a pressure equivalent to an oxygen partial pressure of 0.5 MPa; meanwhile, the tank was heated to the temperatures of 373.15 K or 413.15 K. After four or five hours, a final adjustment in pressure was made. During equilibration, agitation inside the tank was continued so as to mix the solution and the oxygen thoroughly. The total pressure at equilibrium was the sum of the oxygen partial pressure 0.5 MPa and the vapour pressure of the solution at the experimental temperature.

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. One 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 temperature for more than one month before it became unsatisfactory for further use. After this time period, the peanut oil became somewhat viscous and discoloured. It was then replaced with a fresh oil. For safety reasons and some degree of vaporization and odour, the high pressure and temperature absorption part of the equipment was mounted in a fume hood.

When equilibrium was achieved, the desorption of the oxygen-saturated solution was undertaken.

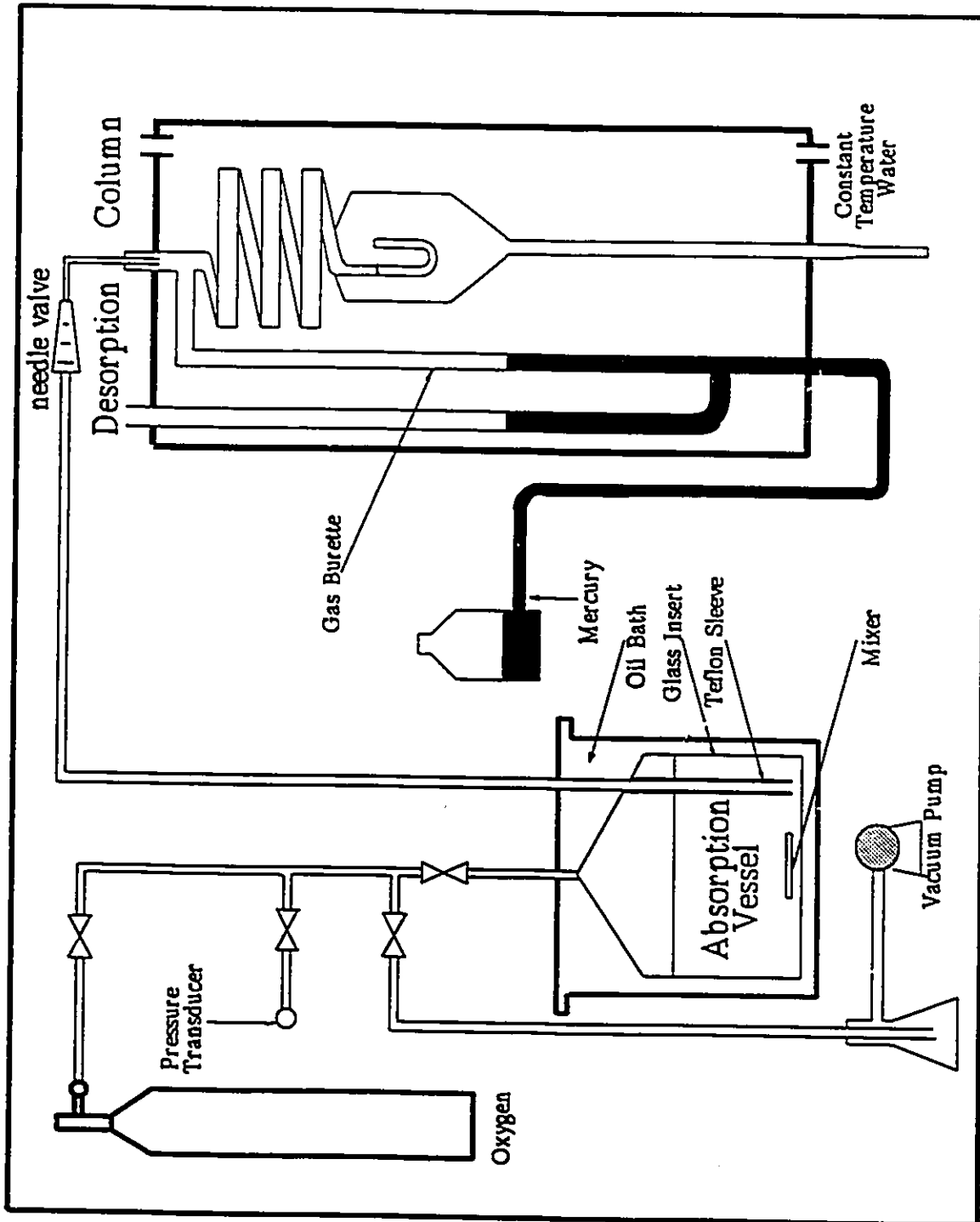


Figure 4 Solubility Equipment for High Pressure

3-5-2 Desorption Procedure at lower Temperature and Pressure

After equilibrium absorption at the elevated temperatures and pressures, the solution was delivered to the desorption apparatus so as to release the oxygen at the atmospheric pressure, and a temperature of 313.15 K. The apparatus used for this purpose is shown in Figure 4. Prior to the desorption, the desorption apparatus was flushed with pure oxygen. Next, the saturated solution was slowly transferred at a constant rate through a flow control valve (needle valve) to the desorption apparatus while maintaining a constant pressure in the high pressure vessel. To obtain a steady flow of the solution in the desorption apparatus, the solution was allowed to flow at least 20 minutes before any measurement was taken. The oxygen which had been dissolved in the high pressure vessel was released in the desorption apparatus, since the pressure inside the desorption apparatus was reduced to atmospheric pressure. The released oxygen was quantitatively collected in the gas burette over mercury. As the quantity of the released oxygen increased, the pressure gradually rose inside the gas burette and spiral coil of desorption apparatus. Therefore, a mercury lift machine driven by a variable speed motor was started and controlled to lower the level of the mercury inside the oxygen burette, so that the pressure inside the burette was kept constant atmospheric pressure.

When steady flow conditions were achieved, the quantity of oxygen released

at 313.15 K and atmospheric pressure at any particular time was determined by reading the volume directly from the gas burette. The corresponding volume of solution from which the oxygen was released was measured in a graduated cylinder. In this desorption process, several pairs of the data of oxygen and solution volumes (at least ten) were collected at regular successive time intervals. Meanwhile, the whole process of the desorption operation, from the beginning to the end, was operated at atmospheric pressure and at a temperature of 313.15 K. The collected data of oxygen and solution volumes were used in the calculation of oxygen solubility in the solution.

3-6 The Principle of the Calculation for the Solubility Result

All experiments of the oxygen solubilities were classified into two catalogues: the oxygen solubility at lower temperatures and pressures and those at higher temperatures and pressures. In both instances, the experimental data which were obtained at the lower temperatures and atmospheric pressure were utilized in the calculations. Even though for those experiments conducted at higher pressures and temperatures was absorption, the experimental data which was finally collected were for a lower temperature and atmospheric pressure. Therefore, a P-V-T relation in gas phase can be applied in the calculation for making necessary material balances.

In the calculation of oxygen solubility at lower temperatures and atmospheric pressure, the temperatures for experimental data were 298.15 K, 313.15 K, 333.15 K and 353.15 K. In those at high pressure, the temperature was 313.15 K.

3-6-1 The Calculation at Lower Temperature and Pressure

At each temperature, the volumes of absorbed gas corresponding to the volumes of residual solution were obtained at regular time intervals. From these experimental data, the gas solubility data were obtained in volume (ml) of

absorbed gas per volume (ml) of residual solution by using a least squares method.

In most papers, however, the gas solubility is expressed as the mole fraction dissolved gas corresponding to gas partial pressure of 101.3 kPa. Therefore, a transformation was done.

As mentioned in the experimental procedure, a total pressure equivalent to one atmosphere was applied to the solubility measurement. The total pressure included the partial pressure of oxygen and the vapour pressure of solution at the experimental temperature. Meanwhile, the volume measured of pure oxygen was measured at the experimental pressure in the gas burette. Therefore, to obtain the number of the moles of the oxygen dissolved in a given time interval, a P-V-T equation for gas phase was used as follows:

$$P V_{O_2} = z n_{O_2} R T \quad (19)$$

From the above equation, the amount of absorbed oxygen expressed as the number of moles was then calculated at the partial pressure of the experiment. Next, the amount of absorbed oxygen expressed in the number of moles was calculated at the partial pressure of 101.3 kPa.

At lower pressure, the Henry's law constant of oxygen in water is approximately independent of pressure (see the chapter of Results and Discussion):

$$K_{O_2} = \frac{x_{p_{O_2}=1atm}}{p_{O_2} (= 1 atm)} = \frac{x_{O_2}}{p_{O_2}} \quad (20)$$

In the above equation,

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O} + \dots} \quad (21)$$

Since the solubility of oxygen in water is very low, the number of moles in the denominator of Equation 21, n_{O_2} , could be neglected. Equation 20 is then transformed into:

$$\frac{n_{p_{O_2}=1atm}}{p_{O_2} (= 1atm)} = \frac{n_{O_2}}{p_{O_2}} \quad (22)$$

If p_{O_2} is expressed in atm, the above equation becomes:

$$n_{p_{O_2}=1atm} = \frac{n_{O_2}}{p_{O_2}} \quad (23)$$

In the above equation,

$$p_{O_2} = P - \alpha_w p_w^o \quad (24)$$

A basis of the number of moles of oxygen dissolved in 100 ml of the

solution was chosen to calculate the oxygen solubility. The number of moles in 100 ml of the solution was obtained from the sum of the number of moles of salt, acid and water contained in 100 ml of the solution. Therefore, the mole fraction was calculated as follow:

$$x_{o_2} = \frac{n_{o_2}}{n_{o_2} + n_{H_2O} + n_{H_2SO_4} + n_{Cu^{2+}} + n_{Ni^{2+}}} \quad (25)$$

The calculated results are shown in Appendix B-2.

3-6-2 The Calculation at Higher Temperature and Pressure

In this instance, the experimental data were obtained by using a least squares method between the volumes of gas released, rather than absorbed, and the volumes of residual solution.

The volume of gas obtained included the volume of oxygen and the volume of evaporated water from the solution at the operating temperature of 313.15 K. Therefore, the actual number of moles of oxygen was obtained by substituting the partial pressure of oxygen and the total volume of gas in a P-V-T equation for the gas phase, rather than by substituting the measured volume of gas. The P-V-T equation is expressed as follows:

$$p_{O_2} V_t = z n_{O_2} R T \quad (26)$$

From the above equation, the number of moles of oxygen was obtained from the experimental data of the volume and partial pressure of oxygen.

A basis of the number of moles of oxygen dissolved in 100 ml of the solution was chosen to calculate the solubility. The number of moles of 100 ml in the solution was obtained from the sum of salt, acid and water contained in 100 ml of the solution.

The solubility of oxygen in mole fraction is then calculated as follows:

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O} + n_{H_2SO_4} + n_{Cu^{2+}} + n_{Ni^{2+}}} \quad (27)$$

The solubility obtained in this way did not include the solubility of oxygen at the temperature of 313.15 K, in which the oxygen was released. To compensate for the calculated oxygen solubility at high temperature and pressure, the volume of oxygen in the solution at pressure of 101.3 kPa and temperature of 313.15 K was added to the value of the oxygen solubility at the high temperature and pressure. The calculated results are shown in Appendix B-3.

3-7 Measurement of Vapour Pressures of the Aqueous Electrolyte Solutions

As described previously, vapour pressures of aqueous electrolyte solution play an important role in the determination of solubilities of oxygen in the aqueous electrolyte solutions. Therefore, equipment was designed for this purpose. For the measurement of the vapour pressures of the aqueous electrolyte solutions, a stainless steel pressure vessel was equipped with a stirrer. An accurate, absolute pressure transducer was calibrated and used to measure the vapour pressures.

3-7-1 Description of Equipment for the Measurement of Vapour Pressures

The container used for the vapour pressure determination consisted of a stainless steel pressure vessel with a capacity of 200 ml. A glass container was placed inside the pressure vessel to prevent the corrosion of the stainless steel vessel by sulphuric acid. A stirrer bar was used to improve liquid-gas mixing.

The pressure measuring system was an accurate, absolute pressure transducer (MKS Instrument.) which consisted of a transducer and a digit readout indicator. Using this instrument, the absolute pressure could be measured to ± 0.5 mmHg.

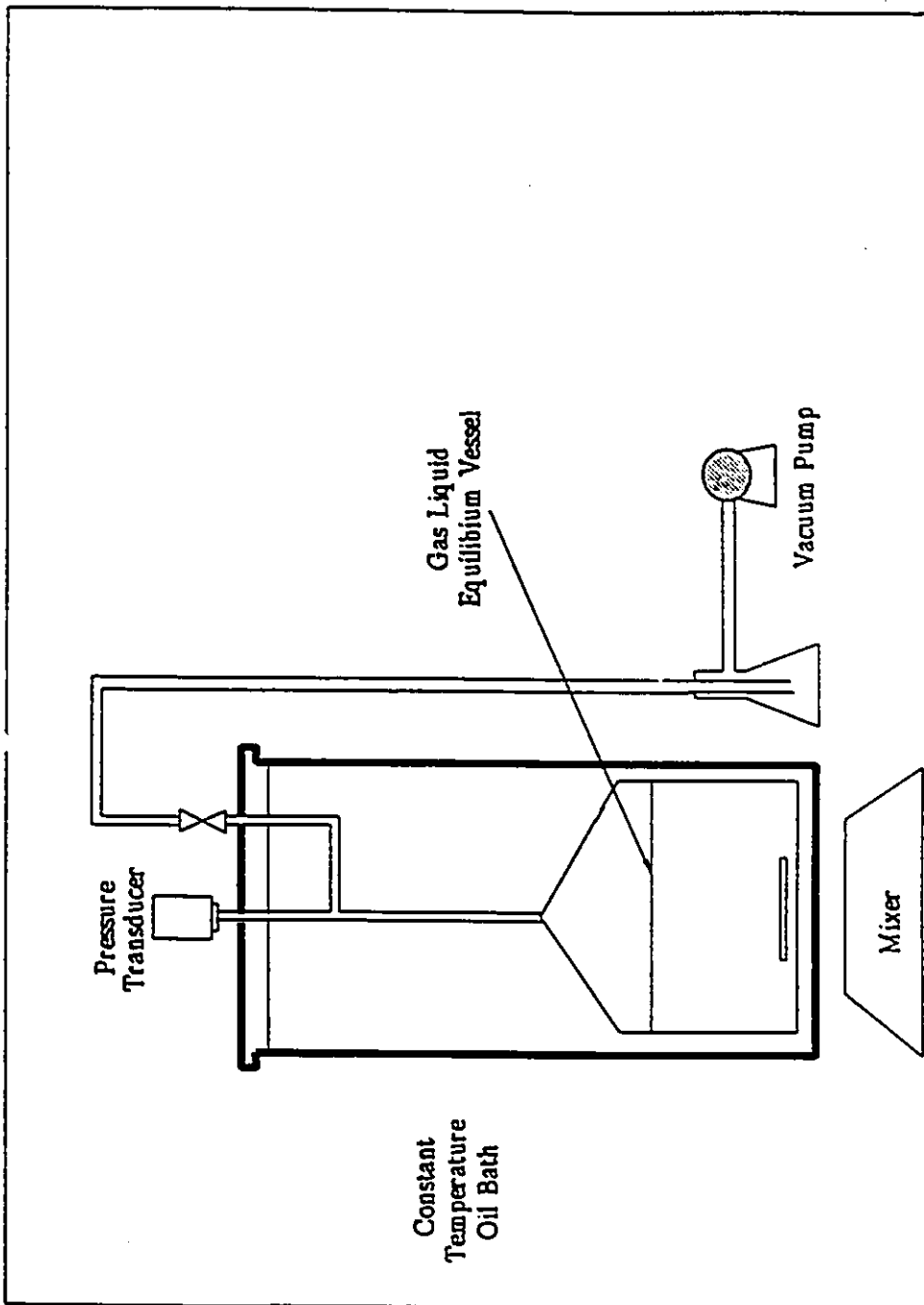


Figure 5 Equipment for the Measurement of Vapour Pressure of Aqueous Electrolyte Solution

3-7-2 Procedure

The vessel was charged with about 100 cm³ of water or electrolyte solution and then sealed. The solution was degassed at room temperature. Degassing was achieved by means of a vacuum pump, while the solution was being agitated by a magnetic stirrer. The purpose of stirring was to accelerate the degassing.

When the solution had been degassed at ambient temperature, the valve connecting the vacuum pump to the vessel was closed. The container was then immersed in the oil bath at the experimental temperature. At the same time, the pressure inside the vessel was monitored by means of the pressure transducer. At first, the pressure changed with time, because the water in the solution inside the container was vaporized as more heat was added to the solution. Finally, the pressure became constant. At this time, it was considered that vapour-liquid equilibrium was reached at this temperature. The pressure displayed on the pressure monitor represented this vapour-liquid equilibrium pressure, that is, the vapour pressure of the measured solution. Each experiment took from half to two hours, depending on the vapour pressure to be measured.

For these measurements, it was considered that the distance between the transducer and the oil surface in the oil bath needed to be as small as possible. Practice showed that this section of the connecting tube greatly affected the results of the measured vapour pressure, especially at higher temperatures. It was considered that the temperature in this section of tubing was normally lower than

that of the oil bath. To overcome this disadvantage, a layer of fibre glass insulation was used to cover the outside of the tube in this section. This treatment effectively prevented the heat loss so that a reliable vapour pressure was obtained even at the higher temperatures.

3-7-3 Calibration of Transducer for Vapour Pressure Measurement

For slight variations of measured vapour pressure from the actual vapour pressures of distilled water, a minor adjustment to the calibration of instrument was required. The instrument was calibrated by comparing the measured vapour pressures with actual vapour pressures of distilled water which were published by Perrys (1984). The vapour pressures are shown in Appendix C.

4. RESULTS AND DISCUSSION

In this chapter, oxygen solubilities in water and aqueous sulphuric acid solutions containing copper and/or nickel ions at various experimental temperatures and pressures are discussed. The densities of the solutions, which were used in the determination of oxygen solubilities, are also discussed.

It was found from the experimental data that the logarithm of oxygen solubility in aqueous sulphuric acid solutions, containing bivalent cations of copper and nickel, are linearly related to the densities of the solutions. As an extension of this relationship, a simple model is suggested. Using this model, oxygen solubilities in aqueous acid-salt solutions in this research can be predicted based on the densities of the solutions and oxygen solubilities in water at various temperatures for the oxygen partial pressure of 101.3 kPa. Compared with other models, this model has an advantage, since the parameter used in this model is independent of solution temperature and mole concentration of bivalent cations in the solution in the range of experimental concentrations and temperatures. The effects of temperatures on oxygen solubilities in water and the aqueous acid-salt solutions were investigated. In general, the results show that oxygen solubilities in the solutions follow the same pattern as those in water and are less affected by temperature as the electrolyte concentration is increased. The effects of pressure

on oxygen solubilities are also discussed.

4-1 The Solubilities at Atmospheric Pressure and Temperatures from 298.15 K to 353.15 K

In this work, the oxygen solubilities in water and the aqueous acid-salt solutions were measured at temperatures from 298.15 K to 353.15 K. The aqueous acid-salt solutions utilized included sulphuric acid solution having a concentration of 150 g/l and two additional solutions having the same acid concentration but containing cupric cations of respectively 30 g/l and 45 g/l. In addition, another solution utilized was an acid solution containing 150 g/l of sulphuric acid, 45 g/l of cupric cation and 15 g/l of nickel cation. The purpose of these experiments was to measure the oxygen solubilities, and to study the effects of temperature and the concentration of bivalent cations Cu^{++} and Ni^{++} on the solubilities of oxygen in these aqueous solutions. The experimental results of oxygen solubility at atmospheric pressure in water and the other aqueous solutions are shown in Appendix B-2 and in Figure 6.

The results for oxygen solubilities in water at all temperatures were found to correspond to published data (Battino, 1981), the largest deviation from those results being 1.5%. Therefore, the results of our experiments are considered to be reliable.

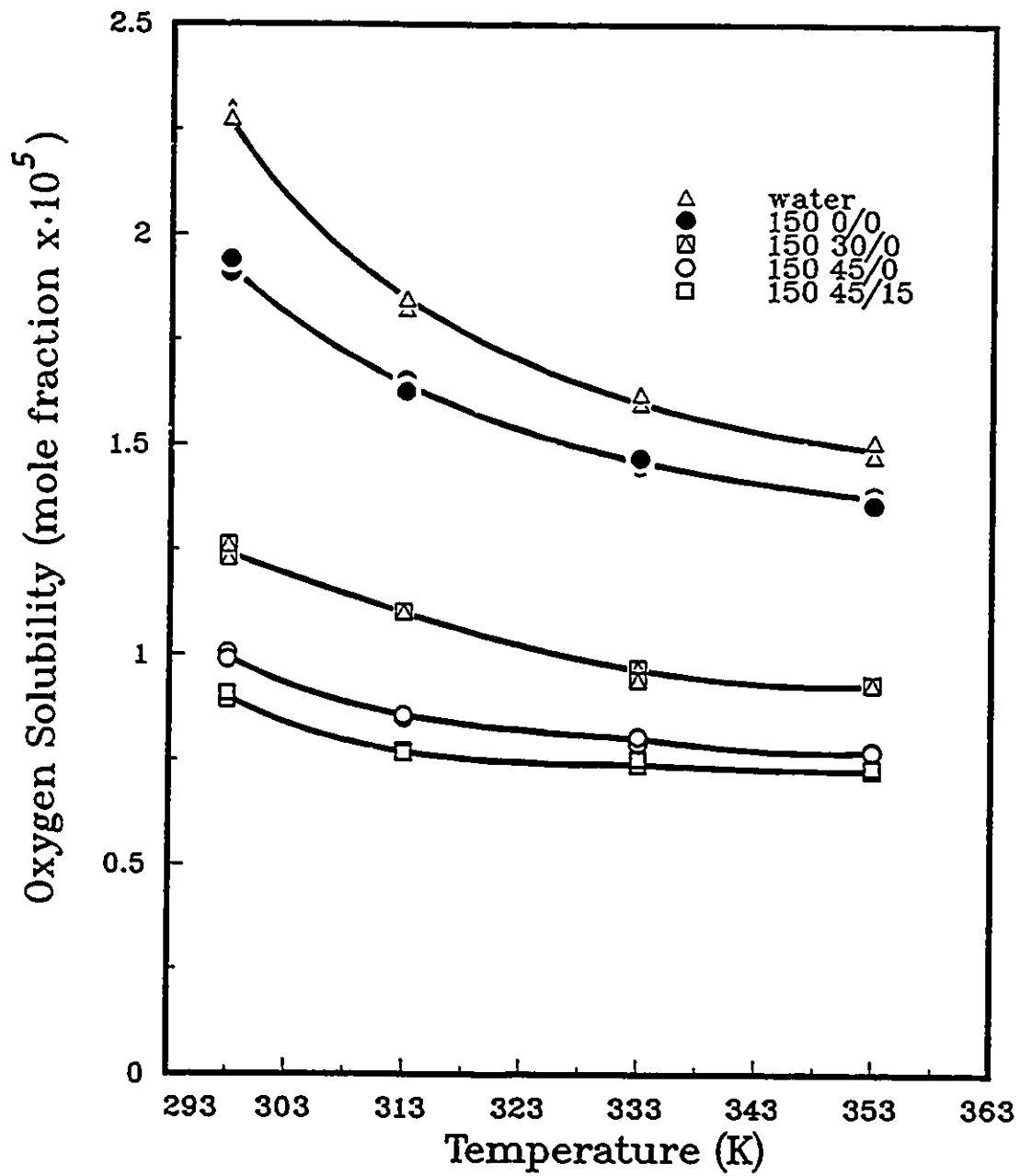


Figure 6 Mole Fraction Oxygen Solubility in Water and Aqueous Acid-Salt Solutions at Atmospheric Pressure

The effect of temperature on solubility is shown in Figure 6. As expected, it is found that the solubility decreases with an increase in temperature. Similarly, the solubilities of oxygen in the aqueous acid and the aqueous acid-salt solutions as a function of temperature follows the same pattern as that in water but are less effected by temperature as the electrolyte concentration is increased, as shown in Figure 6.

4-1-1 The Effects of Cations Cu^{++} and Ni^{++} on the Oxygen Solubility in Aqueous Sulphuric Acid Solutions

The effects of sulphuric acid and/or metallic sulphate salts on the oxygen solubilities in water are shown in Figure 6. All the electrolytes used (sulphuric acid, copper sulphate and nickel sulphate) caused a decrease in the solubilities of oxygen when compared with the oxygen solubility in water. This tendency can be clearly seen by looking at the variation of the Setschenow salt effect parameters presented in Appendix D. These values were calculated using the total electrolyte concentration of each solution and the Bunsen coefficient in water for the corresponding conditions. The Setschenow salt effect parameters increased with an increase in concentration of salt contained in solution or, correspondingly, the oxygen solubility decreased with an increase in concentration of salt contained in the solution. This phenomenon may occur because the addition of salt causes the weakening of the molecular interaction between oxygen and water, resulting in a

lower solubility of oxygen. Therefore, oxygen is salted out by sulphuric acid and the acid-salt solutions.

Generally, the acid-salt solutions may affect the solubility of oxygen as described above. To better understand this relationship, a graph was plotted to find the characteristics of this phenomenon.

Figure 7 shows the relation between the solubility of oxygen and the mole concentration of the bivalent cations Cu^{++} and Ni^{++} in sulphuric acid having a concentration of 150 g/l. In Figure 7, a mole concentration of bivalent cation of zero corresponds to an aqueous sulphuric acid solution containing 150 g/l of the acid. The mole concentrations in mol/l of 0.48 and 0.72 correspond to the cupric ion concentrations of 30 g/l and 45 g/l, and the mole concentration of 0.96 corresponds to the combined concentration of 45 g/l of copper and 15 g/l of nickel.

As shown in Figure 7, the solubility of oxygen is a gradually decreasing function of the mole concentration of bivalent cations Cu^{++} and Ni^{++} . It is noted that oxygen is "salted out" by increasing the concentrations of Cu^{++} and Ni^{++} in the sulphuric acid solution with a concentration of 150 g/l. The relationship between oxygen solubility and the concentration of bivalent cations is found to be linear when expressed as the logarithm of oxygen solubility and the mole concentration of bivalent cations at various temperatures except for the highest salt concentration, as shown in Figure 8.

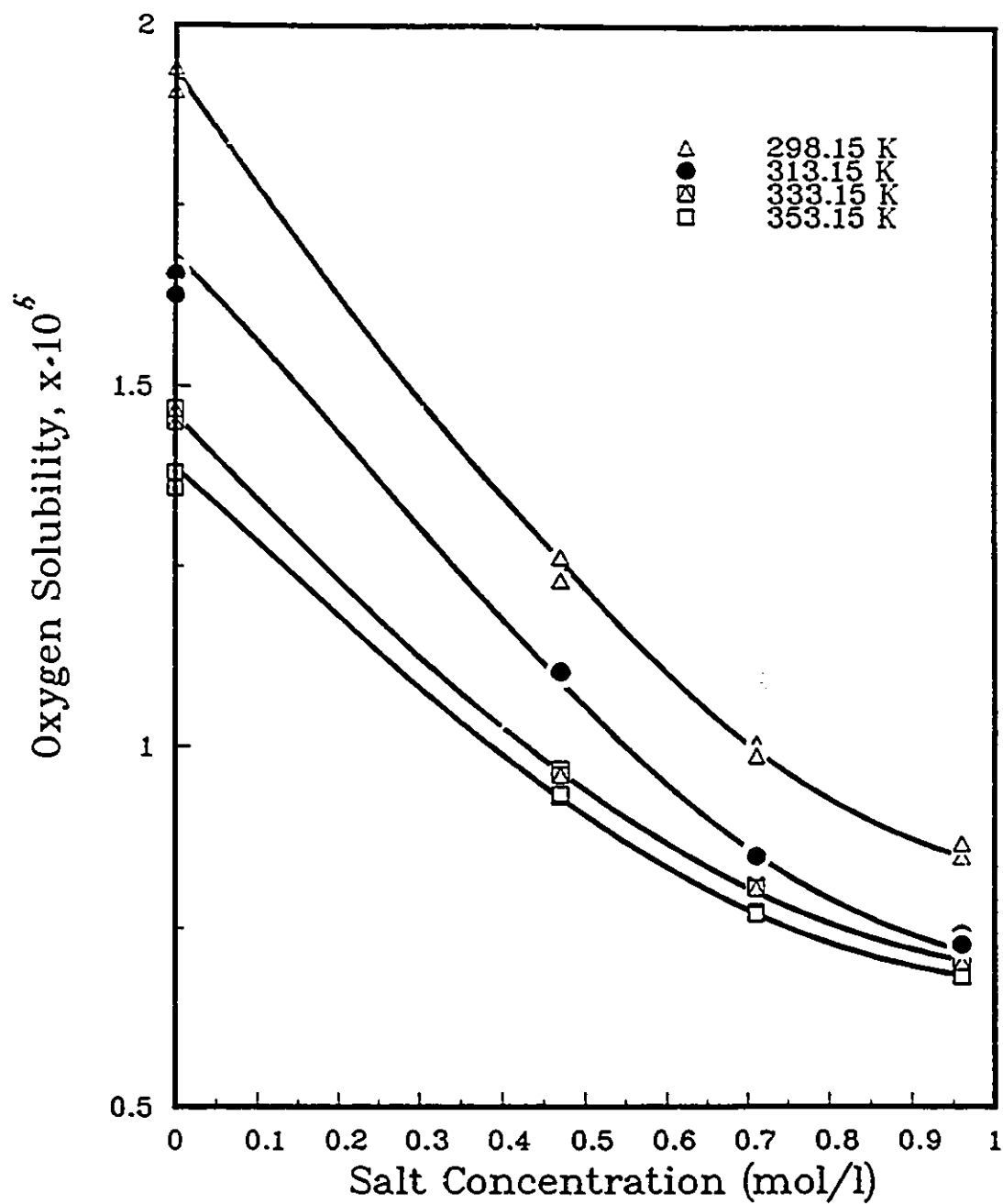


Figure 7 Oxygen Solubility versus Concentration of Dissolved Salts

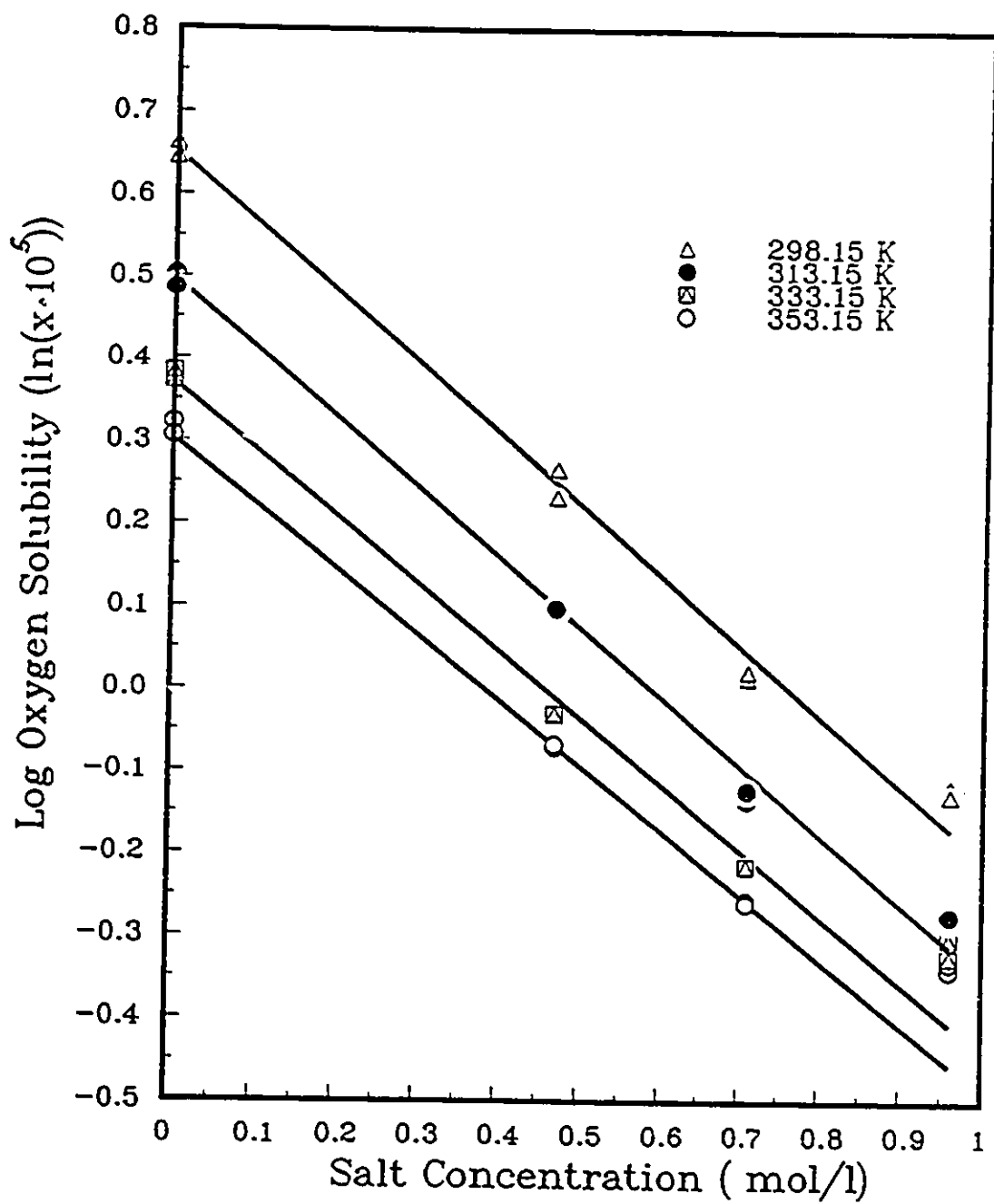


Figure 8 Logarithm of Oxygen Solubility versus Concentration of Dissolved Salts

For temperatures from 298.15 K to 353.15 K, the solubilities of oxygen in aqueous sulphuric acid solutions containing either dissolved Cu^{++} or Ni^{++} are decreased in the presence of either of these ionic salts. Furthermore, it is found that the effect of added nickel ions on the salting out of oxygen is less than that of added copper ions.

As shown in Figure 8, the rates of salting out of oxygen can be represented by the slopes of the lines, which represents the effect of added amounts of metallic salt on oxygen solubility in the aqueous sulphuric acid solutions. The effect of temperature on the degree of salting out oxygen is also shown in Figure 8. It is noted that the slopes of the lines decrease with increasing temperature. This phenomenon suggests that the effect of added salts is to displace the oxygen from the acid solutions. However, the influence of temperature in this case is small.

4-1-2 Densities of Aqueous Acid-Salt Solutions

The densities of the acid-salt solutions were measured at 298.15 K using the precision vibration-reed density meter. At temperatures from 313.15 K to 413.15 K, the measurements were carried out in dilatometers where the dilation of the solution inside the pyrex glass capillary tubes was accurately measured by using a cathetometer. The experimental results of densities are presented in Appendix A.

No comparison for the densities of the acid-salt solutions used here are

available from earlier publications. Therefore, distilled water was used for calibration of the density meter and dilatometers.

The results for densities of the solutions as a function of temperature are shown in Figure 9. It may be observed from Figure 9 that the densities are a decreasing function of increasing temperature. This corresponds essentially to the thermal expansion of the liquid solutions. Furthermore, the decrease in density is least at lower temperatures and it becomes larger at higher temperatures. At the same time, the decrease in solution densities of the acid-salt solution, follows the same pattern as that for distilled water.

The effect of concentration of the bivalent cations copper and nickel on the densities is also shown in Figure 9. It is found that the densities increase with an increase in the concentration of the cations copper and nickel. To better understand this effect, a graph was drawn to find the relationship between the solution densities and the concentration of bivalent cations copper and nickel, as shown in Figure 10. The definition of mole concentration in Figure 10 is same as that in Figure 7. It is found from Figure 9 that the linear relationship occurs in the acid solution containing the bivalent cation, copper. When 15 g/l of nickel is added into the acid solution, the density is lower than that of copper. It may be observed from Figure 10 that the slope of the line decreases slightly with an increase in temperature. It is indicated that the effect of concentration of bivalent cations on the densities of the solutions decreases with an increase in temperature.

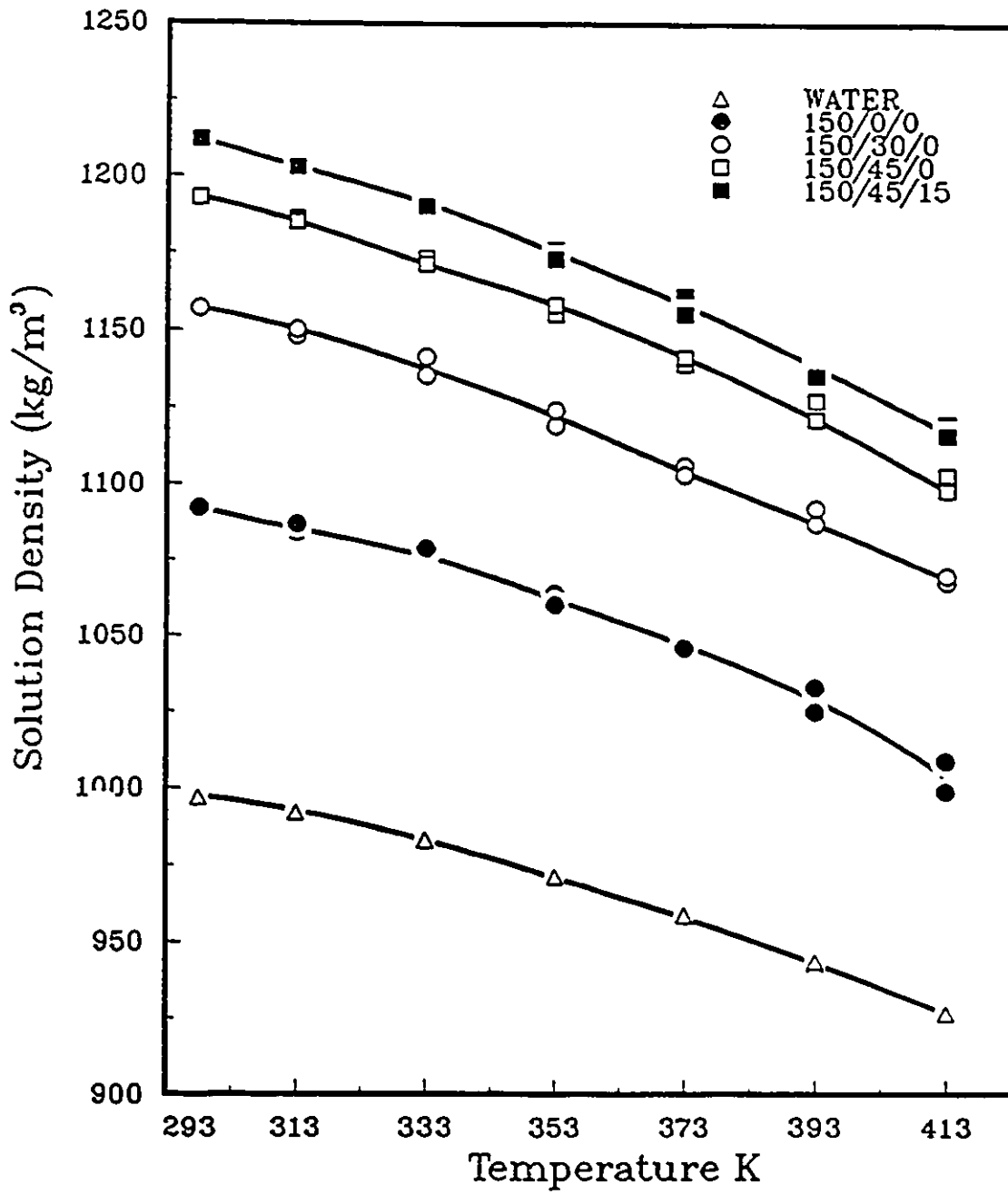


Figure 9 Densities of the Aqueous Acid-Salt Solutions versus Temperature

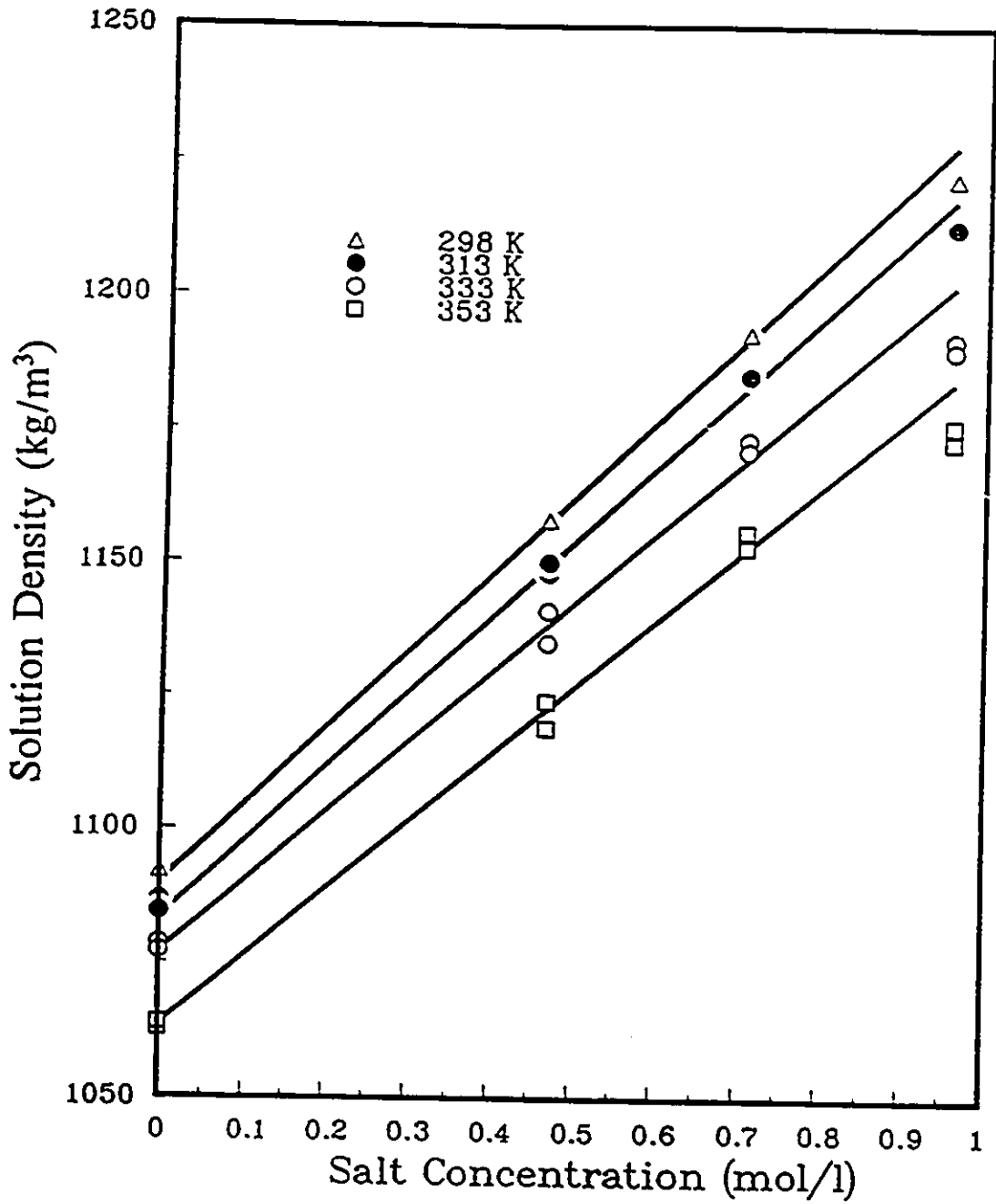


Figure 10 Solution Density versus Salt Concentration in the Acid-Salt Solutions

4-1-3 The Relation between Solution Density and Oxygen Solubilities in Aqueous Sulfuric Acid Solutions Containing Copper and/or Nickel Ions

As described above, the relationship between oxygen solubility and concentration of the bivalent cations was found to be linear, as shown in Figure 8. Meanwhile, the relationship between solution densities and concentration of the bivalent cations was also linear, as shown in Figure 10. To better understand the relation between these variables, the logarithm of the oxygen solubilities were plotted against the solution densities for different temperatures, as shown in Figure 11. It may be observed that the logarithm of the oxygen solubility decreases linearly with an increase in the density of the solution at various temperatures in all instances in which copper ions are present in the acid solution. When 15 g/l of nickel ions are added to the acid solution containing copper ions, however, the relation between the logarithm of the oxygen solubility and the density of the acid-salt solutions is different at lower temperatures from that at higher temperatures.

At the lower temperatures of 298.15 K and 313.15 K, the relation between the logarithm of the oxygen solubility and the density of the acid-salt solutions containing Cu^{++} and Ni^{++} are described by the same relationship as that between the oxygen solubility and the density of the acid solution containing only copper ions. This result suggests that the oxygen solubility in the acid solution might be

independent of the type of the bivalent cations which are dissolved in the solution; it appears to depend only on the density of the solution. However, at the temperatures of 333.15 K and 353.15 K, the oxygen solubilities in the acid solution, containing 45 g/l of copper and 15 g/l of nickel, are not described by the same relationship as that between the logarithm of the oxygen solubility and density of the acid solution containing only cation copper. In the acid solution containing bivalent cations of both copper and nickel, it appears that for the same concentrations dissolved nickel reduces the oxygen solubilities in the solution less than that for dissolved copper.

In Figure 11, it is also found that the slopes of lines are approximately the same at temperatures from 298.15 K to 353.15 K. This indicates that the effects of the density of the acid-salt solution on the oxygen solubility are the same at these temperatures. This result is very helpful in establishing a new simple model to predict the oxygen solubilities as a function of solution density.

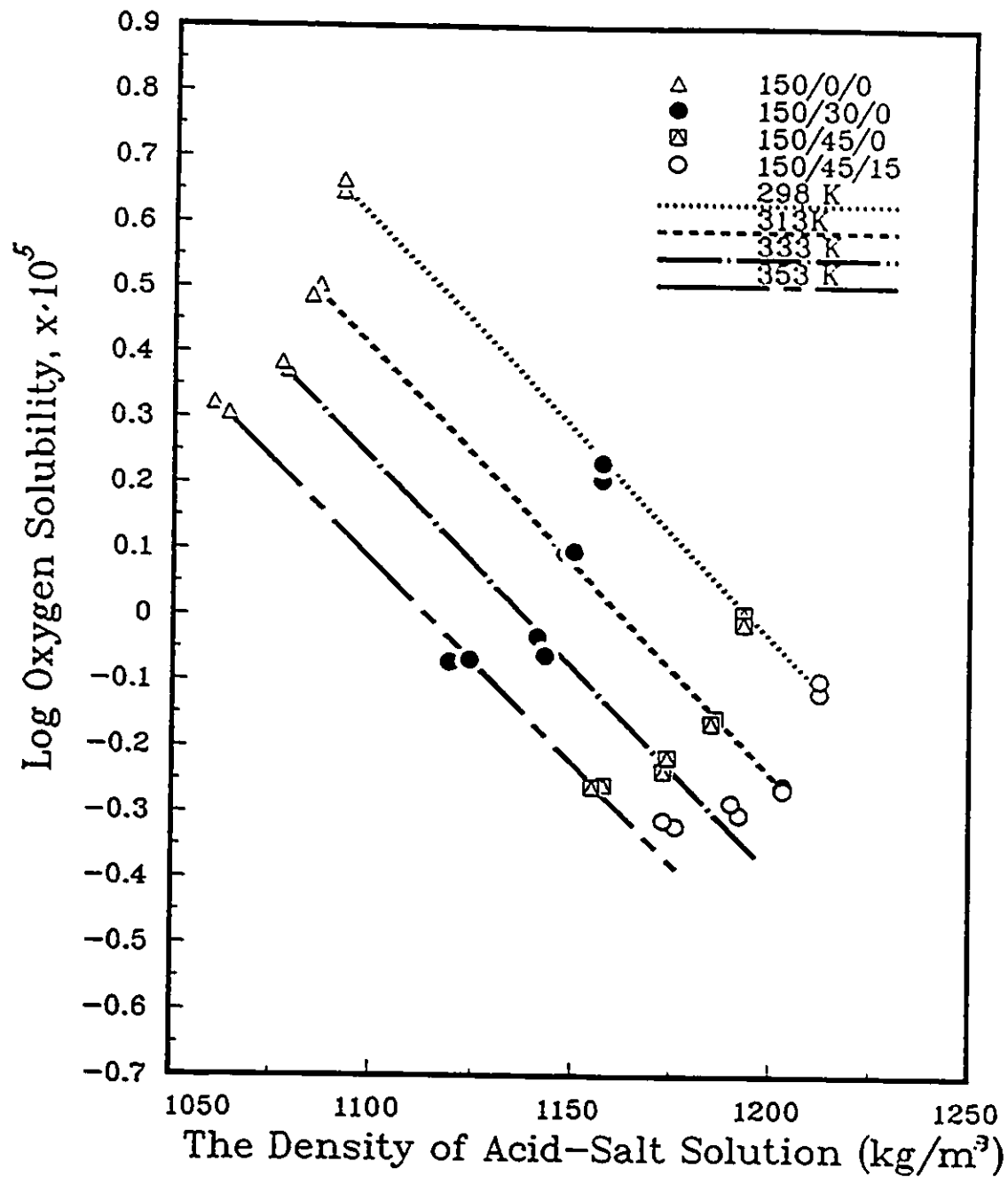


Figure 11 The Logarithm of Oxygen Solu-
 bility in the Acid-Salt Solutions
 versus the Solution Density

4-1-4 A New Simple Model to Predict the Oxygen Solubility in Aqueous Acid-Salt Solution

As described above, the relationship between solubilities and densities is linear at temperatures from 298.15 K to 353.15 K. It is also found from Figure 11 that the slope of all these lines are approximately the same. From Figure 11, the linear relation between the oxygen solubilities and the densities of the acid and salt can be expressed as follow:

$$\ln S_{salt} = \ln S_{acid} + a(\rho_{salt} - \rho_{acid}) \quad (28)$$

In the above equation, 'a' is the slope of the straight line. Therefore, when the oxygen solubility in the acid solution and density of the acid-salt solution are obtained at a known temperature, the oxygen solubility in the acid-salt solution can be estimated by using the above equation. It is noted that because the slope is constant for all temperatures, the parameter 'a' is also a constant. The above equation, therefore, provides a simple method to predict the oxygen solubility in the acid-salt solution if the density of the acid-salt solution is known. To be useful, however, Equation 28 needs the oxygen solubilities in acid solutions. These can be determined indirectly from the relation of the oxygen solubility in

acid solutions and in water so that the oxygen solubilities in the acid-salt solution can be estimated. Both the oxygen solubility in water and in the acid solutions have been measured in this work, as found in Appendix B. The ratio of the oxygen solubility in the acid solution to that in water can be calculated as follow:

Table 1 The ratios of oxygen solubilities in the acid solution to that in water

Temperature (K)	298.15	313.15	333.15	353.15
The ratio of solubilities	.89	.92	.93	.92

From Table 1, it is found that the ratios of the oxygen solubilities at different temperatures are approximately the same. Therefore, the ratio of the solubilities can be applied in Equation 28 to describe the oxygen solubility in the acid solution. The result is as follow:

$$\ln S_{salt} = \ln (0.92 S_w) - a (e_{acid} - e_{salt}) \quad (29)$$

or

$$\ln\left(\frac{S_{salt}}{S_w}\right) = \ln 0.92 - a (e_{acid} - e_{salt}) \quad (30)$$

Using this method, the oxygen solubility in the acid-salt solution can be estimated. The constant, a , is $5.77(\text{cm}^3/\text{g})$. The standard deviation of the results is 2.89 % from the equation.

4-1-5 Comparison of the Models

As described in the Chapter entitled Theoretical Aspect, gas solubilities in electrolyte solutions can be estimated by the models of Setchenow (1892) and Krevelen and Hofijzer (1948). In these models, the relation between the electrolyte concentration or ionic strength and gas solubility in the electrolyte solution is described. These models have been widely applied for the prediction of gas solubility, especially the model of Setchenow. However, the parameters in these models are dependent on the temperature and the concentration of the electrolytes in the electrolyte solution.

In Setchenow model, gas solubility can be estimated based on total electrolyte mole concentration. Therefore, the effect of different electrolyte on gas solubility cannot be observed from this model. For example, in the case of an electrolyte solution containing two electrolytes, such as H_2SO_4 and CuSO_4 , the gas solubility is only dependent on the total electrolyte concentration. From this model, we cannot tell the different effects of H_2SO_4 and CuSO_4 on gas solubility. In addition, the Setchenow salt effect parameter in this model, as shown in Appendix D, is a decreasing function of temperature and salt concentration. Gas

solubility can be obtained at a known temperature and concentration of electrolyte (or electrolytes), only when the Setchenow salt effect parameter is known at the corresponding temperature and concentration. For example, the solubility in the acid solution at a temperature of 313.15 K can be calculated only by applying the Setchenow salt effect parameter in the acid solution at the temperature of 313.15 K.

To overcome this disadvantage, Krevenlen and Hoftijzer developed the ionic strength model. In this model, expressed by Equation 14, the different effects of electrolytes on gas solubility are represented by the different contributions of the electrolytes to the reduction of gas solubility in water. Therefore, the contributions of different ions on gas solubility can be found so as to extend these values to other electrolyte concentrations. Therefore, in the calculation of gas solubility, the parameters, expressing the ionic contributions, are independent of the ionic concentration. However, the parameters of gas contributions on the solubility depends on temperature. Therefore, a number of contributions for anyone gas at different temperatures need to be obtained before the gas solubility can be estimated by this model. Until now, there have been few published data of gas contributions, and most of them are at the temperatures of 288 K and 298 K. Therefore, a great deal of work needs to be done to develop this model for a wide range of temperatures and for different gases.

Compared with the two models mentioned above, the model suggested in

this research has some advantages. Firstly, the parameter 'a' represents the constant slope of the logarithm of the oxygen solubility and density at different temperatures in a range of this research. Therefore, in a range of temperatures from 298.15 K to 353.15 K, there is one value of the slope. Secondly, the effects of different electrolytes on the reduction of the oxygen solubility are also represented in this model. For example the first term in Equation 30 represents the effect of sulphuric acid on the oxygen solubility and the second term represents the effect of salt sulphate on the oxygen solubility. Thirdly, the same parameter in this model is used to calculate the oxygen solubility at different temperatures and ionic concentrations.

4-2 The Oxygen Solubilities in Water and Aqueous Acid-salt Solutions at Elevated Temperatures and a Pressure of 0.5 MPa

The oxygen solubilities in water and aqueous acid-salt solutions at elevated temperatures and a pressure of 0.5 MPa were measured in this research. The acid solution used in the experiment contained 150 g/l of sulphuric acid. One acid-salt solutions containing 150 g/l of sulphuric acid and 45 g/l of copper ions, and the other contained 200 g/l of the acid and 45 g/l of copper ions. The experimental results for the oxygen solubilities in water and in the acid-salt solutions at the pressure of 0.5 MPa and the temperatures from 373.15 K to 413.15 K are shown

in Appendix B-3.

As published by Battino (1981), the oxygen solubilities in water at a pressure of 101.3 kPa are 1.444×10^{-5} and 1.599×10^{-5} mole fraction at the temperatures of 373.15 K, and 413.15 K, respectively. In this research, the oxygen solubilities in water at the pressure of 0.5 MPa were found to be 7.18×10^{-5} , and 7.96×10^{-5} , mole fraction for the same respective temperature, which are almost exactly 5 times that at the pressure of 101.3 kPa. Therefore, the oxygen solubility in water closely obeys Henry's law.

The oxygen solubilities in the acid-salt solutions were measured only at the pressure of 0.5 MPa, so that the effect of the pressure on the oxygen solubility in the solution was not directly observed. However, the work of Kimweri (1990) showed that the oxygen solubility in the sulphuric acid leach solutions containing zinc ions obeys Henry's law at different pressures. This phenomenon is also explained by the following equation:

$$\frac{d (\ln K_{O_2})}{d P} = \frac{d \ln\left(\frac{x_{O_2}}{P_{O_2}}\right)}{d P} = \frac{v_{O_2}}{R T} \quad (31)$$

When Equation 31 is integrated, the following equation results:

$$\ln \frac{K_{o_2,1}}{K_{o_2,2}} = \frac{v_{o_2}}{R T} \Delta P \quad (32)$$

The values of v_{o_2} are 0.18068 cm³/mole, and 0.1846 cm³/mole at the temperatures of 278.15 K, and 358.15 K, respectively, (Battino, 1981). Based on this information, it may be concluded that the partial molar volumes v_{o_2} at the temperatures of 373.15 K and 413.15 K are less than 0.2 cm³/mol. Hence, the right side of the Equation 32 is only 0.0003, and as a result, the ratio of Henry's law constants at a pressure difference of 0.5 MPa is close to 1. That is, in the range of this research, the oxygen solubilities in the aqueous acid-salt solutions obey Henry's law.

4-3 The Effect of Temperature On Oxygen Solubility in Water and Aqueous Acid-Salt Solution

Oxygen solubilities in water and aqueous acid-salt solutions as a function of temperature at the partial pressure of 101.3 kPa are shown in Figure 12. The oxygen solubilities at temperatures from 298.15 K to 353.15 K are given in Appendix B-2. The oxygen solubilities at the temperatures of 373.15 K and 413.15 K were obtained by using Henry's law and the oxygen solubilities at the partial pressure of 0.5 MPa, as shown in Appendix B-3.

It is found from Figure 12 and Appendix B-2 and B-3 that oxygen solubilities in water and aqueous acid-salt solutions are decreasing functions of temperature below 353.15 K. However, they are increasing functions of temperature above 373.15 K. Therefore, there are minimum solubilities in these solutions at temperatures between 353.15 K and 373.15 K. These phenomena were also observed by other people(Hayduk et al., 1973).

The effect of sulphuric acid and the acid-salt in the leach solutions can be observed in Figure 12. Generally, the addition of the acid and acid-salt mixture reduces the solubility of oxygen when compared with that in water. At any temperature, there is greater reduction of the oxygen solubility when the concentration of the acid or acid-salt mixture is increased.

4-4 General Discussion

The completion of this research represents a number of contributions to the measurement of chemical engineering data. A number of technical innovations for the equipment for solubility measurement as well as improvement to the measurement of other solution properties were developed. A double jacketed solubility apparatus made it possible to precisely control the temperature even at 353 K. The whole equipment could be successfully operated with concentration of sulphuric acid up to 150 g/l and temperature up to 353.15 K. A two-step method (absorption-desorption) was successfully used in solubility measurement at higher pressures and temperatures. For these measurements, equipment needed to be constructed of stainless steel for the measurements at high pressure, but allowance was necessary to prevent seriously corrosion of the equipment by the acid at high temperatures. To effectively operate experiments at high temperatures and pressures, a number of technologies for protecting the stainless steel from possible erosion-corrosion attack were applied in this experiment. In particular, a glass beaker was inserted in the equipment cell and Teflon tube was used to withdraw the acid solutions at elevated temperatures and pressures. Since the acid solution at high temperature could corrode the expensive densitometer, an alternate device, the dilatometer, was developed for measuring the densities of acid

solutions. The vapour pressure of acid solutions was measured by using a pressure transducer, by means of which the absolute pressure was obtained. All the equipment used in this research was tested or calibrated by using distilled water.

CONCLUSIONS

1. Oxygen solubilities in aqueous sulphuric acid-copper and nickel sulphate solutions has a minimum solubility at a temperature of about 368 K.
2. A marked reduction of oxygen solubilities is observed at all temperatures as the amount of dissolved copper or nickel sulphate is increased in the aqueous solutions.
3. The densities of all solutions are decreasing functions of temperature.
4. The experimental results indicate that the logarithm of oxygen solubilities is a linear function of the solution densities and the slope of the line is constant at temperatures from 298.15 K to 353.15 K. A new simple model is then suggested as follow:

$$\ln \frac{S_{salt}}{S_W} = \ln \frac{S_{acid}}{S_W} + a (e_{Acid} - e_{salt}) \quad (33)$$

5. Compared with the other models (Setchenow, ionic strength), the model suggested in this research has some advantages. That is, the parameter a in the model is independent of temperature and salt concentration.

6. The oxygen solubilities in water closely obey Henry's law in a range of the experimental pressures (≤ 5 atm).

REFERENCES

- Battino, R. and H.L. Clever, "The Solubility of Gases in Liquids", *Chem. Rev.*, **66**, 395-463 (1966).
- Battino, R., *IUPAC Solubility Data Series: Oxygen and Ozone*, Vol. 7, Pergamon Press (1981).
- Benson, B.B., D.Jr. Krause and M.A. Peterson, "The Solubility and Isotopic Fractionation of Gases in Dilute Aqueous Solution: I. Oxygen", *J. Solution Chem.*, **8**, 655-690 (1979).
- Bruhn, G., J. Gerlach and F. Pawlek, *Zeit. Anorg. Allg. chem.*, **68**, 337 (1965)
- Chengfang, Zhang, Gas-Liquid Reaction and Reactors, *Chemical Industry Press*, Beijing (1985).
- Choundry, V.R., M.G. Parande and P.H. Brahme, "Simple Apparatus for Measuring Solubility of Gases at High Pressures", *Ind. Eng. Chem. Fundam.*, **21**, 472-474 (1982).
- Clever, H.L. and R. Battino, in *Solutions and Solubilities*, Ed. M.R.J. Dack, John Wiley, New York (1975).
- Danckwerts, P.V., *Gas-Liquid Reaction*, McGraw-Hill, New York (1970).

- Fogg, P.G.T. and W. Gerrard, *Solubility of Gases in Liquids: a critical evaluation of gas/liquid systems in theory and practice*, John Wiley, London, 1-38 (1990).
- Gerrard, W., *Solubility of Gases and Liquids*, Plenum Press, New York (1976).
- Hayduk, W., H. Asatani and Y. Miyano, "Solubilities of Propene, Butane, Isobutane and Isobutene Gases in n-octane, Chlorobenzene and n-Butanol Solvents", *Can. J. Chem. Eng.*, **66**, 466 (1988).
- Hayduk, W., E.B. Walter and P.J. Simpson, "Solubility of Propane and Carbon Dioxide in Heptane, Dodecane, and Hexadecane", *J. Chem. Eng. Data*, **17**, 59-61 (1972)
- Hayduk, W. and H. Laudie, "Solubilities of Gases in Water and Other Associating Solvents", *AICHE J.*, **19**, 1233 (1973).
- Holmes, H.F. and R.E. Mesmer, "Isopiestic Studies of H₂SO₄(aq) at elevated temperatures", *J. Chem. Thermo.*, **24**, 317-328 (1992).
- Horvath, A.L., *Handbook of Aqueous Electrolyte Solutions*, John Wiley, New York (1985).
- Hu, Y., X. Yingnian and J.M. Prausnitz, "Molecular Thermodynamics of Gas Solubility", *Fluid Phase Equilibria*, **23**, 15-40 (1985).
- Hu, Y., X. Yingnian and J.M. Prausnitz, "Molecular Thermodynamics of Gas

- Solubility(III): Henry's Constants of Gases in 1-1 Type Electrolytic Solutions", *J. Chem. Ind. and Eng. (Chinese)*, 2, 146-155 (1987).
- Japas M.L. and J.M.H.L. Sengers, "Gas Solubility and Henry's Law Near the Solvents Critical Point", *AIChE J.*, 35, 705 (1989).
- Jun-Shun, Y., Chiang Yung-Yi, Shy Der-Shin and Tsai Fuan-Nan, "Solubilities of Carbon Dioxide in Carboxylic Acids Under High Pressure", *J. Chem. Eng. Japan*, 25, 544-548 (1992).
- Levine, I.N., *Physical Chemistry*, McGraw-Hill, New York, 227-280 (1983).
- Morrison, T.J. and F.J. Billet, "The Measurement of Gas Solubilities", *J. Chem. Soc.*, 2033-2035 (1948).
- Perry, R.H., *Perry's Chemical Engineer's Handbook*, McGraw-Hill, 6th Edition (1984).
- Prausnitz, J.M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall Englewood Cliffs, N.J. (1969).
- Smith, J. M. and H. C., Van Ness, *Introduction to Chemical Engineering Thermodynamics*, Fourth Edition, McGraw-Hill (1987).
- Whilhelm, E., R. Battino and R. Wilcock, "Low-Pressure Solubility of Gases in Liquid Water, *Chem. Rev.*, 77, 219-261 (1977).

Appedix A

The Densities of Solutions from 298.15 K to 413.15 K

A-1 Densities of Water, Methanol and Solution at 298.15 K

Solution	Frequency	Density [g/cm ³]
Water	0.777793 ± 0.000005	0.99704
Methanol	0.737120 ± 0.000002	0.78664
150/0/0	0.795836 ± 0.000002	1.0921
150/30/0	0.807702 ± 0.000007	1.1567
150/45/0	0.817731 ± 0.000007	1.1934
150/45/15	0.817731 ± 0.000009	1.2121

A-2 Lengths of the solution columns in dilatometer tubes, m,
for temperatures from 25 °C to 140 °C

solution		25°C	40°C	60°C	80°C	100°C	120°C	140°C
water	1	.40043	.40244	.40612	.41040	.41474	.41895	.42580
	*				1.0016	1.004	1.008	1.012
	2	.41579	.41761	.42144	.42600	.43106	.43667	.44267
	*				1.0014	1.003	1.007	1.010
150/0/0	3	.32477	.32705	.32876	.33287	.33719	.34365	.35225
	*				1.0015	1.004	1.008	1.011
	4	.40095	.40296	.40589	.41240	.41737	.42969	.43813
	*				1.0015	1.003	1.009	1.012
150/30/0	1	.40835	.41087	.41383	.41953	.42649	.42864	.43601
	*				1.0016	1.004	1.009	1.012
	2	.41405	.41726	.42182	.42726	.43183	.43713	.44404
	*				1.0014	1.003	1.007	1.010
150/45/0	1	.39804	.40091	.40577	.40935	.41451	.42003	.42573
	*				1.0016	1.004	1.009	1.012
	2	.41919	.42189	.42649	.43253	.43800	.44036	.45024
	*				1.0014	1.003	1.007	1.010
150/45/15	3	.33305	.33560	.33935	.34350	.34803	.35299	.35735
	*				1.0015	1.004	1.008	1.011
	4	.41944	.42257	.42668	.43177	.43644	.44315	.44860
	*				1.0015	1.003	1.009	1.012

* the expansion factor of the tube

A-3 The densities of solutions at the temperatures from 25°C to 140°C

	water	150/0/0	150/30/0	150/45/0	150/45/15
25°C	0.99704	1.092	1.157	1.193	1.212
25°C	0.99704	1.092	1.157	1.193	1.212
40°C	0.9922	1.084	1.150	1.185	1.203
40°C	0.9922	1.086	1.148	1.185	1.203
60°C	0.9832	1.077	1.141	1.171	1.190
60°C	0.9832	1.078	1.135	1.173	1.192
80°C	0.9718	1.064	1.124	1.158	1.173
80°C	0.9718	1.060	1.119	1.155	1.176
100°C	0.9584	1.047	1.103	1.141	1.155
100°C	0.9584	1.047	1.106	1.139	1.161
120°C	0.9431	1.025	1.092	1.121	1.135
120°C	0.9431	1.033	1.087	1.127	1.137
140°C	0.9261	0.999	1.070	1.103	1.116
140°C	0.9261	1.008	1.068	1.098	1.120

Appendix B

Oxygen Solubilities in the Solutions

B-1 The Oxygen Solubilities in ml Oxygen/100ml solution

	25°C	40°C	60°C	80°C
water	2.988	2.424	1.938	1.230
	3.016	2.395	1.971	1.252
150/0/0	2.480	2.080	1.743	1.160
	2.440	2.120	1.720	1.179
150/30/0	1.686	1.475	1.193	0.823
	1.642	1.471	1.160	0.826
150/45/0	1.354	1.166	1.028	0.704
	1.376	1.176	1.009	0.699
150/45/15	1.249	1.058	0.948	0.673
	1.225	1.064	0.967	0.668

B-2

The Oxygen Solubilities in Mole Fraction($\times 10^5$)
at Atmospheric Pressure

	25°C	40°C	60°C	80°C
water*	2.293	1.867	1.586	1.478
water	2.277	1.847	1.599	1.476
	2.299	1.824	1.622	1.510
150/0/0	1.941	1.626	1.468	1.358
	1.909	1.655	1.450	1.380
150/30/0	1.262	1.103	0.941	0.931
	1.230	1.100	0.969	0.935
150/45/0	0.989	0.850	0.806	0.770
	1.005	0.857	0.790	0.773
150/45/15	0.908	0.768	0.753	0.733
	0.892	0.773	0.739	0.726

* Battino, 1981

B-3 Oxygen Solibilities at 5 atm in mole fraction($\times 10^5$)

	100°C	140°C
water	7.141	7.892
	7.221	7.958
150/0/0	6.545	6.987
	6.121	7.247
150/45/0	3.809	4.636
	3.667	4.553
200/45/0	2.991	3.943
	3.037	4.187

Appendix C

Vapour Pressures of the Solutions

	water*	Water	150/0/0	150/45/0	200/45/0
298.15 K (a)	23.76	25	23	23	23
(b)		23.76	21.86	21.86	21.86
(c)		3.17	2.91	2.91	2.91
313.15 K (a)	55.32	56	52	52	50
(b)		55.32	51.36	51.36	49.4
(c)		7.37	6.85	6.85	6.58
333.15 K (a)	149.4	151	134	131	131
(b)		149.4	132.6	122.6	122.6
(c)		19.91	17.67	16.34	16.34
353.15 K (a)	355.1	356	338	325	315
(b)		355.1	337.0	324.2	314.1
(c)		47.33	44.92	43.21	41.86
373.15 K (a)	760.0	760	708	680	673
(b)		760.0	708.0	680.0	673.0
(c)		101.3	94.37	90.64	89.70
413.15 K (a)	2711.1	2710	2559	2457	2394
(b)		2711.1	2560.0	2458.0	2395.0
(c)		361.4	341.2	327.6	319.2

* Perrys, Handbook of Chem. Eng.

- (a) experimental data, mmHg
- (b) calibrated vapour pressure, mmHg
- (c) calibrated vapour pressure, kPa

Appendix D

The Setschenow Parameters as a Function of Temperature and Solution Composition

solution composition (g/l)	25°C	40°C	60°C	80°C
150/0/0	0.0542	0.0418	0.0326	0.0191
	0.0588	0.0364	0.0363	0.0146
150/30/0	0.1253	0.1134	0.1066	0.0883
	0.1309	0.1172	0.1072	0.0892
150/45/0	0.1543	0.1513	0.1245	0.1098
			0.1282	0.1113
150/45/15	0.1621	0.1522	0.1302	0.1130
	0.1656	0.1510	0.1337	0.1144

Appendix E

SAMPLE CALCULATION

Sample calculations of the amounts of chemicals used to prepare the test solution are explained below. In all calculations, the 150 g/l sulphuric acid solution with 45 g/l copper and 15 g/l nickel was taken as an example and a basis of 1000 ml of solution was used

E-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, 150 grams of pure sulphuric acid were required. The density of the acid was 1830 kg/m³ and the percentage purity was 95.59%.

It means that, 1 m³ of the 95.59% acid contains

$$1 \text{ m}^3 * 0.9559 * 1830 \text{ kg/m}^3 = 1759.3 \text{ kg of pure sulphuric acid}$$

Therefore, 0.15 kg of pure acid can be obtained from:

$$\left(\frac{1 \text{ m}^3}{1759.3 \text{ kg}}\right) * 0.15 = 8.527 * 10^{-5} \text{ m}^3 = 85.27 \text{ ml of sulphuric acid}$$

E-2 The Amount of Copper or Nickel Sulphate

The amount of copper or nickel sulphate required was obtained by using the molecular weight of the hydrated copper or nickel sulphate and the atomic mass of copper or nickel, as well as their purities.

Example: In the solution mentioned before, 45 grams of copper and 15 grams of nickel were needed. The molecular weight of the hydrated copper and nickel sulphates were 249.68 kg/kmol and 262.84 kg/kmol, the atomic mass of copper and nickel are 63.54 and 58.71, and their purities were 99.5 %

Therefore, 63.54 kg of copper are contained in:

$$\frac{1 \text{ kmol} \times 249.68 \text{ kg/mol}}{0.995} = 250.9 \text{ kg of powder}$$

58.71 kg of nickel are contained in

$$\frac{1 \text{ kmol} \times 262.84 \text{ kg/mol}}{0.995} = 264.16 \text{ kg of powder}$$

To get 0.045 kg of copper, the amount of powder needed

$$\frac{250.90 \text{ kg/kmol}}{63.54 \text{ kg/kmol}} \times 0.045 \text{ kg} = 0.17769 \text{ kg}$$

To get 0.015 kg of nickel, the amount of powder needed

$$\frac{264.16 \text{ kg/kmol}}{58.71 \text{ kg/kmol}} \times 0.015 \text{ kg} = 0.06749 \text{ kg}$$

Appendix F

The Calculation of Compressibility Factor for Oxygen, Z(Smith et al., 1987)

The compressibility factor, Z, can be expressed by the second virial coefficient:

$$Z = 1 + \frac{B P}{R T} \quad (1)$$

For a binary mixture,

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12} \quad (2)$$

In the above equation,

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (3)$$

Prausnitz (1969) expanded the second virial coefficient to multi-components:

$$B_{ij} = \frac{RT_{cij}}{P_{cij}} (B^0 + w_{ij} B^1) \quad (4)$$

In the above equation,

$$w_{ij} = \frac{w_i + w_j}{2} \quad (5)$$

$$T_{cij} = (T_{ci} T_{cj})^{\frac{1}{2}} \quad (6)$$

and

$$P_{cij} = \frac{Z_{cij}RT_{cij}}{V_{cij}} \quad (7)$$

Here,

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \quad (8)$$

$$V_{cij} = \left(\frac{V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}}{2} \right)^3 \quad (9)$$

$$(10)$$

In the Equation 4

$$B^0 = 0.083 - \frac{0.422}{(T/T_c)^{1.6}} \quad (11)$$

$$B^1 = 0.139 - \frac{0.172}{(T/T_c)^{4.2}} \quad (12)$$

Substituting equations 4, 11 and 12 into Equation 1, the second virial coefficient can be obtained. The compressibility factor, Z, is then calculated by Equation 1.

Appendix G

A Least Square Method used for Data Regression

For a function,

$$f = \sum (y_i - (a + bx_i))^2$$

In the above equation, a and b are the intersection and slope of regression line. x_i and y_i are experimental data. In the case of oxygen solubility, x_i and y_i are the volumes of solution and oxygen.

To achieve a minimum of the function, f,

$$\frac{\partial f}{\partial a} = 2 \sum (y_i - (a + bx_i))(-1) = 0$$

$$\frac{\partial f}{\partial b} = 2 \sum (y_i - (a + bx_i))(-x_i) = 0$$

By solving the above equation, a and b are obtained as follows:

$$a = \frac{\sum y_i \sum x_i^2 - \sum x_i y_i \sum x_i}{n \sum x_i^2 - \sum x_i \sum x_i}$$

$$b = \frac{\sum y_i \sum x_i^2 - \sum x_i \sum (y_i x_i)}{n \sum x_i^2 - (\sum x_i)^2}$$

In the above equation, n is the number of experimental data. A programming C

is provided for this purpose. Subroutine, calcu, is edited for least square method.

A sample result is shown in Figure 13.

C Program for Regression of Experimental Data and the Calculation of Mole Fraction Solubility of Oxygen

```
#include <stdio.h>
#include <string.h>
#include <stdlib.h>
#include <conio.h>

#define Size 25

File *fpin, *fout;
Char name1, name2;
float temperature, pressure, vapour_pressure, partial_pressure;
float density, con_hso, con_cu, con_ni, mw_wat, mw_hso, mw_cu, mw_ni;
float wat_mole_num, oxy_mole_num, hso_mole_num, cu_mole_num;
float ni_mole_num, oxy_mole_fraction, volume, z, R;

struct data_oxygen
{ float gas;
  float liq;
} datao[Size];

struct data_conversion
{ float x;
  float y;
} data[Size];
```

```

int main(void);
void input();
void conversion();
void calcu(float *,float *);
void output;

```

```

int main( )
{
    float inte, slop;
    input();
    conversion();
    calcu(&inte,&slop);
    output(&inte,&slop);
    return(1);
}

```

```

void input ( )
{
    int c;
    if((fpin = fopen("a:\\data", "r")) !=NULL) {
        fscanf(fpin, "%s %s", name1, name2);
        fscanf(fpin, "%d %d %d %d", &number, &year, &month, &day);
        fscanf(fpin, "%f %f %f", &temperature, &pressure, &z);
        fscanf(fpin, "%f %f %f", &density, &vapour_pressure, &R);
        fscanf(fpin, "%f %f %f", &con_hso, &con_cu, &con_ni);
        fscanf(fpin, "%f %f %f", &mw_wat, &mw_hso, &mw_cu);
        fscanf(fpin, "%f", &mw_ni);
        for ( c = 0; c < number; c++ ) {
            fscanf(fpin, "%f %f", &datao[c].gas, &datao[c].liq);
        }
        fclose(fpin);
    }
}

```

```

void conversion( )

```

```

{
    int c;
    float x[Size],y[Size],xc[Size],yc[Size];
    for ( c = 0; c < number; c++) {
        x[c] = datao[c].liq;
        y[c] = datao[c].gas;
    }
    for ( c = 0; c < number; c++) {
        xc[c] = x[c];
        yc[c] = y[0] - y[c];
    }
    for ( c = 0; c < number; c++) {
        data[c].x = xc[c];
        data[c].y = yc[c];
    }
}

void calcu(float *aa, float *bb)
{
    int i;
    float x[Size], y[Size];
    float a,b,c,d;

    a = 0.0; b = 0.0; c = 0.0; d = 0.0;
    for ( i = 0; i < number; i++) {
        a = a + y[i]; c = c + x[i]*y[i];
        b = b + x[i]; d = d + x[i]*x[i];
    }

    *aa = (a*d - c*b)/(d*Size - b*b);
    *bb = (c*Size - a*b)/(d*Size - b*b);
}

void output(float *cc, float *dd)

```

```

{
  int c;
  float xc[Size],yc[Size],xx[Size],yy[Size];
  float ab,cd,temp;
  ab = *cc; cd = *dd;
  partial_pressure = pressure-vapour_pressure;
  volume = cd;
  oxy_mole_num = pressure*volume/(R*temperature*z);
  oxy_mole_num = oxy_mole_num/partial_pressure;
  wat_mole_num = density - con_hso - con_cu - con_ni;
  wat_mole_num = wat_mole_num/mw_wat;
  hso_mole_num = con_hso/mw_hso;
  cu_mole_num = con_cu/mw_cu;
  ni_mole_num = con_ni/mw_ni;

temp=wat_mole_num+hso_mole_num+cu_mole_num+ni_mole_num;
  oxy_mole_fraction = oxy_mole_num/(oxy_mole_num + temp);

  fout = fopen("output","w");
  fprintf(fout,"oxygen mole fraction%e\n",oxy_mole_fraction);
fclose(fout);
}

```

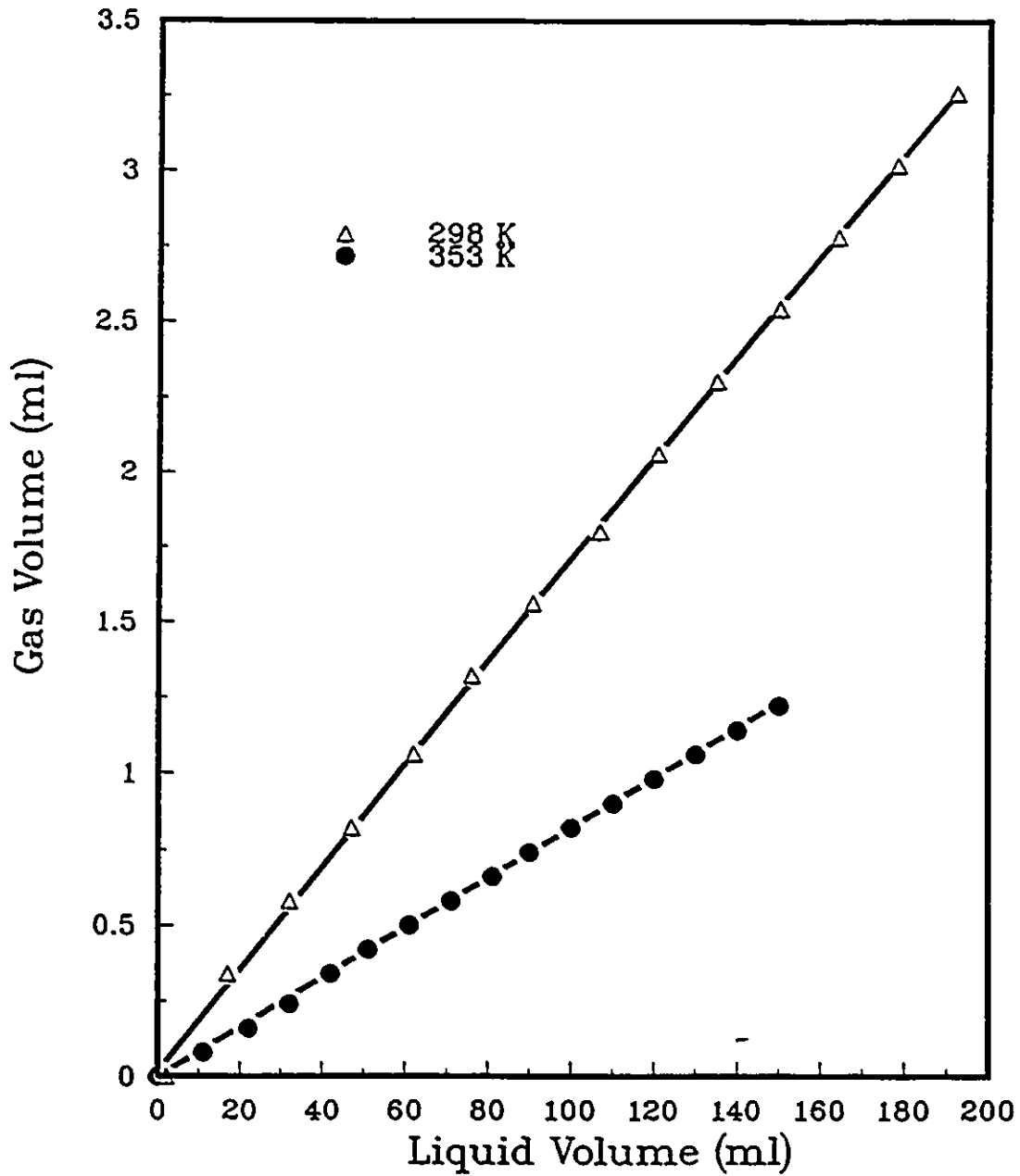


Figure 13 Plot of the Volumes of Gas versus Volumes Of Solution for a Solution Containing 150g/L Acid, 30 g/L Copper Ions