SOLUBILITY OF OXYGEN IN SYNTHETIC PRESSURE LEACHING SOLUTIONS

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ABSTRACT

Solubilities of oxygen in aqueous sulphuric acid containing zinc and ferric sulphate at temperatures of 368, 398 and 428 K at oxygen partial pressures of 405.3, 709.3 and 1013 kN/m^2 and pressures of 202.7, 405.3 and 709.3 kN/m^2 at temperature of 458 K were measured. In addition, solubilities of oxygen were measured in a concentrated solution of zinc sulphate containing 0.3 kg/m^3 of surfactant lignosol and in an industrial sample obtained from the pressure leaching unit of Cominco at Trail, British Columbia, Canada. Oxygen solubilities in the former were measured at 398 K. The solubilities of oxygen from air in the two solutions were determined at air partial pressures of 405.3, 709.3 and 1013 kN/m^2 and temperature of 428 K.

A two-stage method for determination of the solubility, consisting of a high pressure and high temperature absorption step, and an atmospheric pressure desorption step at 323 K, was developed and used. Solutions were first saturated with oxygen at high pressures and temperatures and then, the volumes of oxygen desorbed at 323 K and atmospheric pressure were measured. The experimental results indicated that the solubilities of oxygen in the tested solutions conform with Henry's law. The oxygen solubilities were found to be very low, in the order of 10^{-5} mole fraction at oxygen partial pressure of 101.3 kN/m^2. The addition of sulphuric acid, zinc sulphate and iron sulphate was found to significantly decrease the oxygen solubilities.

Models expressing effects of solution composition on the oxygen solubilities were developed. The models showed that there is a systematic effect of the concentration of each of the three components on oxygen solubility in the

aqueous solutions.

INTRODUCTION

Few data appear in the literature for the solubility of oxygen in water at temperatures above 100°C and even fewer for the solubility in aqueous sulphuric acid. For example, the analysis of oxygen solubility in water presented in literature[1] at temperatures above 100°C was based on a single study conducted by Stephan et al. (1956)[2] Few workers who measured the solubility of oxygen in aqueous sulphuric acid solutions did not cover sufficient common ranges of concentration and temperature for their data to be adequately tested. The data available are thus, considered tentative only.

In the review of oxygen solubility data done by IUPAC[1], it was found out that by 1980, there were only six recorded sets of measurements for solubility of oxygen in aqueous sulphuric acid solutions. The data are too scattered for a direct comparison by interpolation or extrapolation. However, all the results indicate some systematic behaviour at different conditions. At a given temperature and oxygen partial pressure, the solubility decreases with increasing sulphuric acid concentration. Morever, solubility increases with the increase in the partial pressure of oxygen at a constant temperature and solution concentration.

The solubility of oxygen in aqueous sulphuric acid solutions containing salts was measured by Klyueva (1967)[3] The researcher measured the solubility at oxygen partial pressure of 250 and 1013 kN/m^2 at temperatures of 323, 353, 383, 413, 443 and 473 K. The concentration of the solutions was 0.0125 kmol/m^3 sulphuric acid saturated with either nickel sulphide (NiS_2), copper sulphide (Cu_2S) or cobalt sulphide (CO_4S_3). Unfortunately the actual sulphide concentrations were not given in the paper. The presence of sulphuric acid-metal sulphide solutions decreased the oxygen solubility to less than 50 percent of its solubility in water. The variation of oxygen solubility with temperature and partial pressure of oxygen followed the same trend as that for the plain sulphuric acid solutions.

It should be noted that data on oxygen solubility in aqueous sulphuric acid that are available, were generally obtained early in the century. Also, no data have been found on the solubility of oxygen in aqueous sulphuric acid-zinc sulphate solutions. Hence, most of the work presented here is a new addition to technical literature. The purpose of this investigation was to provide equilibrium data which may be useful in the analysis of the pressure leaching process for the recovery of zinc from zinc sulphide concentrates.

In this paper concentrations of the components will be represented in kg/m^3 (g/dm^3) as in the following example: 5/110/1, the first number representing kg/m^3 of sulphuric acid, the second number representing kg/m^3 of divalent zinc and the third number representing kg/m^3 of ferric or trivalent iron in the aqueous solutions. Furthermore, in describing the solutions, the term "acid" will represent sulphuric acid, "zinc" will represent divalent zinc in the solution and "iron" will represent ferric or trivalent iron in the solution. The solutions were prepared from analytical grade concentrated sulphuric acid, hydrated zinc sulphate and iron sulphate salts in quantities sufficient to give the indicated masses of dissolved metals. Some of the solutions have compositions similar to those used in the pressure leaching process for recovery of zinc from zinc sulphide ores.

EXPERIMENTATION

Experimental Set-up

A two-stage method for measuring the high pressure solubilities at elevated temperatures was used. A similar arrangement was used by Choudhary et al. (1982)[4] for measuring solubilities of gases at high pressure. However, these workers used a different apparatus for the desorption step and they did not describe their autoclave. Oxygen was absorbed at constant temperature and pressure in a high pressure absorber and when saturation was complete, a stream of the saturated solution was directed through a needle valve to a glass desorption apparatus operated at atmospheric pressure and temperature of 323 K.

Details of the equipment used in this work are shown in Fig. 1. A high pressure apparatus that consisted of a stainless steel pressure vessel of 6 x 10^{-4} m^3 (600 ml) capacity equipped with a glass vessel insert or liner to contain solvent and a teflon coated magnetic stirrer bar was used for absorbing oxygen. The apparatus was provided with a high precision transducer system for pressures, readable to 0.01 psi. The high pressure vessel was immersed into an insulated constant temperature oil bath which maintained temperature to within 0.1°C. For the sake of economy, safety and convenience the bath oil was an edible peanut oil. The high pressure part of the apparatus was mounted in a fume hood.

The glass desorption apparatus consisted of a spiral coil through which a supersaturated solvent flowed as a thin film releasing oxygen. The spiral tube apparatus was first proposed by Morrison and Billet (1948)[5], and modified by Hayduk and Cheng (1970)[6] and others. While these workers used the spiral apparatus for absorbing gases to saturate solvents, in this work the apparatus was used for desorbing oxygen from saturated solutions. The coil was connected at the top to a burette, initially filled with mercury, and at the bottom to a small U-tube manometer through which the solvent flowed and which acted as a seal confining the released gas in the spiral coil. The manometer also served as a pressure indicator by comparison with the atmospheric pressure. A motorized screw device driven by a variable speed motor was connected to the apparatus for steady lowering of the mercury level.

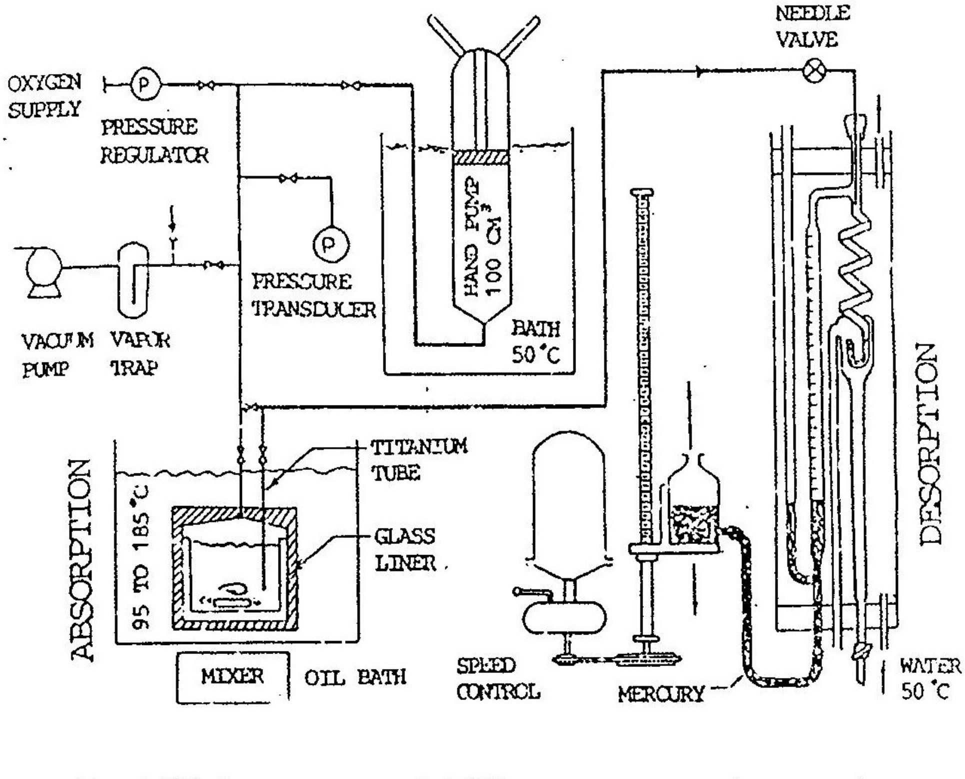


Fig. 1 High pressure solubility measurement apparatus

Experimental Procedure

The pressure absorption vessel was charged with a desired solution and its top was sealed with a teflon gasket. Next, the vessel was placed into the oil bath. After heating for 15 minutes, the solution was deaerated by intermittently purging some of the vapour from the vessel into an ice-cooled vapour trap. Then, the vessel was pressurized with oxygen to a pressure equivalent to the oxygen partial pressure of 1013 kN/m^2 and was equilibrated for several hours. A final adjustment in pressure was made and the equilibration continued for 12 hours. After this time, about 75 ml of the solution saturated with the oxygen was transferred to the desorption apparatus; while maintaining a constant pressure in the high pressure vessel. The quantity of dissolved oxygen was determined at atmospheric pressure and temperature of 323 K. As the pressure in the gas collecting system was gradually increasing, the level of mercury was steadily lowered using the variable-speed motorized screw device. The volume of solvent which was in equilibrium with oxygen at the outlet of the desorption column, was measured using a graduated cylinder. The volume of gas was read directly from the gas burette. About 15 readings of oxygen volume at atmospheric pressure and the corresponding solvent volume were collected for each desorption run. Next, the oxygen pressure was reduced to an oxygen partial pressure of 709.3 kN/m^2. An equilibration period of approximately 2 to 3 hours was required before a second solubility determination was made at the lower pressure.

This procedure was repeated at the oxygen partial pressure of 405.3 kN/m^2. At temperature of 458 K, the pressures chosen for the solubility determinations were 202.7, 405.3 and 709.3 kN/m^2 because of the high vapour pressure of the solutions and the equipment limitation at pressures exceeding 2027 kN/m^2.

After completion, the pressure vessel was removed, rinsed, and recharged for the next solubility determination. It was found that a shorter time was required for achieving saturation from an initially supersaturated condition than that required to equilibrate from an unsaturated solution. It was thus faster to achieve the equilibrium conditions in the high pressure absorber by initially starting at the highest partial pressure of oxygen (1013 kN/N^3), and subsequently reducing the oxygen pressure to 709.3 kN/m^2 and then to 405.3 kN/m^2.

A slight change in procedure was required for solubility determinations using compressed air. During the desorption step of the procedure, a sample of the desorbed gas accumulated in the burette was withdrawn using a syringe and was analyzed using a gas chromatography (GC). In this way the composition and hence, the partial pressure of oxygen as well as the quantity of oxygen released during desorption were determined. The total quantity of oxygen dissolved at high pressure was calculated as the sum of oxygen released at atmospheric pressure and that still dissolved in the solution at atmospheric pressure and temperature of 323 K. Solubility of oxygen at the oxygen pressure of 101.3 kN/m^2 and temperature of 323 K was determined separately by absorption of oxygen in the deaerated solutions in the spiral column at the aforesaid conditions using a procedure given by Hayduk and Laudie (1973)[7]

A computer program was employed to calculate the solubility, Henry's law constant and the Bunsen coefficient (volume of oxygen at STP per volume of solvent). Also calculated was an average Henry's law constant and average gas solubility corresponding to an oxygen partial pressure of one atmosphere, for each solution at each temperature. The magnitude of error in each experiment was also estimated using this program. At least two determinations of oxygen solubility were made for each condition and concentration. Additional replicate were made at higher temperatures (428 and 458 K), because there was some difficulty in obtaining highly consistent results at these temperatures. The inconsistency of results at these temperature was caused by corrosion of the stainless steel tube which produced some gas (probably hydrogen) that interfered with volumetric determination of oxygen. The problem was solved by using ferric (oxidizing) ion to passivate the stainless steel.

RESULTS AND DISCUSSION

Solubility measurement

The oxygen solubilities in the synthetic acid-salt solutions at pressures 1013, 709.3 and 405.3 kN/m^2 of oxygen and temperature of 368 K are presented in Fig. 2. From Fig. 2 it can be seen that the solubility behaviour of the solutions closely conforms to Henry's law at the temperature of 368 K, namely, the solubility increases proportionally to the increase in pressure. Similar behaviour can be observed at other temperatures. Furthermore, Fig. 2 shows a very large reduction in oxygen solubility in the aqueous acid solutions with high zinc concentrations. For the solution containing 110 kg/m^3 of zinc, the oxygen solubility is only about 40% of that in water or dilute (5 kg/m^3) acid. There were also reductions in oxygen solubilities as a result of increase of acid concentrations and increase of iron concentrations in the solutions.

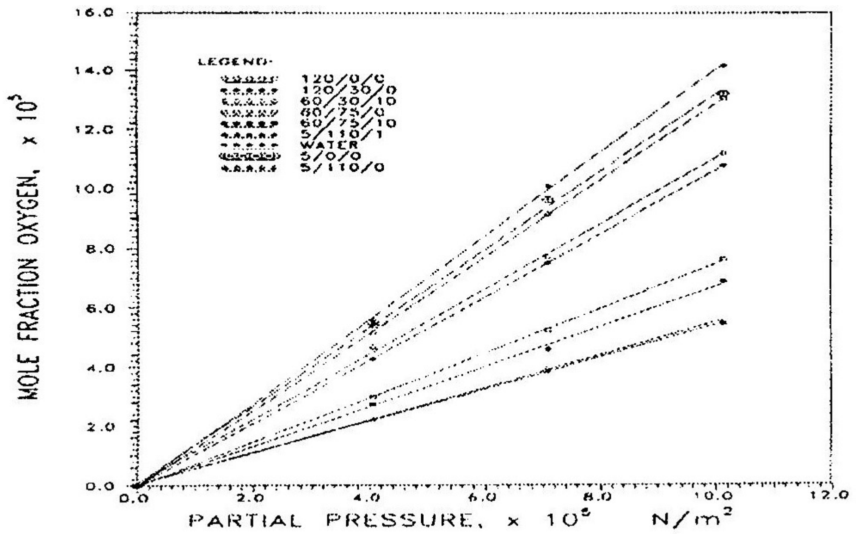


Fig.2: **Mole fraction solubility of oxygen in aqueous sulphuric acid solutions at 368 K**

The average values oxygen solubility at a gas partial pressure of 101.3 kN/m^2 are shown in Table 1. Using Henry's law, the solubilities at the other oxygen partial pressures can be obtained as a multiple of the solubility at a partial pressure 101.3 kN/m^2. The results are also presented graphically in Fig. 3 and Fig. 4. In Fig. 3 and Fig. 4 the mole fraction solubility (x) and oxygen solubility (s) expressed in kg/m^3 respectively are shown. It may be observed that there is a minimum solubility of oxygen in water at about 368 K. The minimum has been reported by Hayduk and Laudie (1973)[7] and it was experimentally observed for water and non- aqueous solvents alike by Prausnitz and Lichtenthaler (1986)[8] Thermodynamic explanation for this phenomenon is given by Beutier and Renon (1978)[9], Schotte (1985)[10], Japas and Sengers (1989)[11] and Harvey and Sengers (1990)[12]. The minimum solubilities were also observed for the various leaching solutions used in this work.

TABLE I: SOLUBILITY OF OXYGEN IN SYNTHETIC SULFURIC ACID LEACH SOLUTIONS FOR AN OXYGEN PARTIAL PRESSURE OF 101.3kN/m^2.

		Temperature, K				
Composition		323	368	398	428	458
120/0/0	s	0.0235	0.0212	0.0227	0.265	0.0325
	$(10^5)x$	1.38	1.27	1.40	1.67	2.11
	$(10^{-3})H$	72.7	78.7	71.4	59.9	47.4
	β	0.0165	0.0148	0.0159	0.0186	0.0228
120/30/0	s	0.0193	0.0175	0.0189	0.224	0.0285
	$(10^{-5})x$	1.13	1.05	1.16	1.41	1.84
	$(10^{-3})H$	88.5	95.2	86.2	70.9	54.3
	β	0.0135	0.0123	0.0132	0.0157	0.0200
60/30/0	s	0.0189	0.0172	0.0186	0.218	0.0277
	$(10^5)x$	1.10	1.03	1.14	1.37	1.79
	$(10^{-3})H$	90.9	97.1	87.7	73.0	55.9
	β	0.0132	0.0121	0.0130	0.0153	0.0194
60/75/0	s	0.0147	0.0131	0.0143	0.177	0.0241
	$(10^5)x$	0.84	0.77	0.86	1.09	1.53
	$(10^{-3})H$	119	130	116	91.7	65.4
	β	0.0103	0.0092	0.0100	0.0124	0.0169
60/75/10	s	0.0133	0.0119	0.0133	0.166	0.0225
	$(10^5)x$	0.76	0.70	0.80	1.02	1.43
	$(10^{-3})H$	132	143	125	98.0	69.9
	β	0.0093	0.0083	0.0093	0.0116	0.0158
5/110/1	s	0.0111	0.0093	0.0106	0.146	0.0209
	$(10^5)x$	0.62	0.53	0.62	0.88	1.30
	$(10^{-3})H$	161	189	161	114	76.9
	β	0.0078	0.0065	0.0074	0.0102	0.0146
water	s	0.0298	0.0243	0.0260	0.298	0.0358
	$(10^5)x$	1.70	1.42	1.56	1.84	2.29
	$(10^{-3})H$	58.8	70.4	64.1	54.3	43.7
	β	0.0209	0.0170	0.0182	0.0209	0.0251
5/0/0	s	0.0294	0.0239	0.0257	0.298	0.0356
	$(10^5)x$	1.68	1.40	1.54	1.84	2.27
	$(10^{-3})H$	59.5	71.4	64.9	54.3	44.1
	β	0.0206	0.0167	0.0180	0.0209	0.0249
5/110/0	s	0.0294	0.0239	0.0257	0.298	0.0356
	$(10^5)x$	1.68	1.40	1.54	1.84	2.27
	$(10^{-3})H$	59.5	71.4	64.9	54.3	44.1
	β	0.0206	0.0167	0.0180	0.0209	0.0249

It should be noted that in the solubility calculations the oxygen was assumed to behave as an ideal gas.

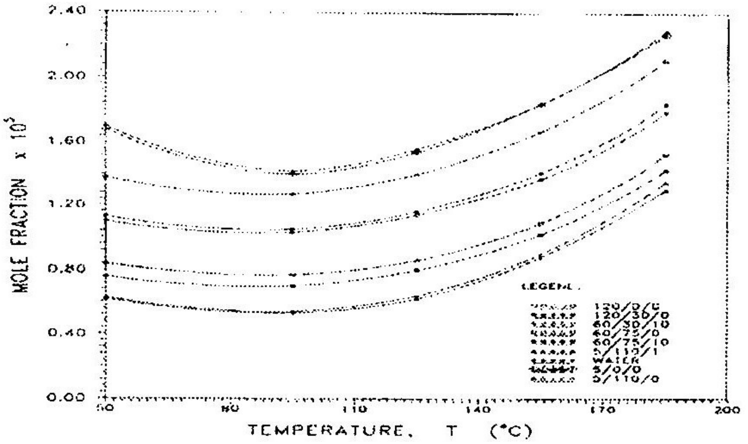


Fig. 3: **Oxygen solubility expressed as mole fraction for partial pressure of 101.3 kN/m2**

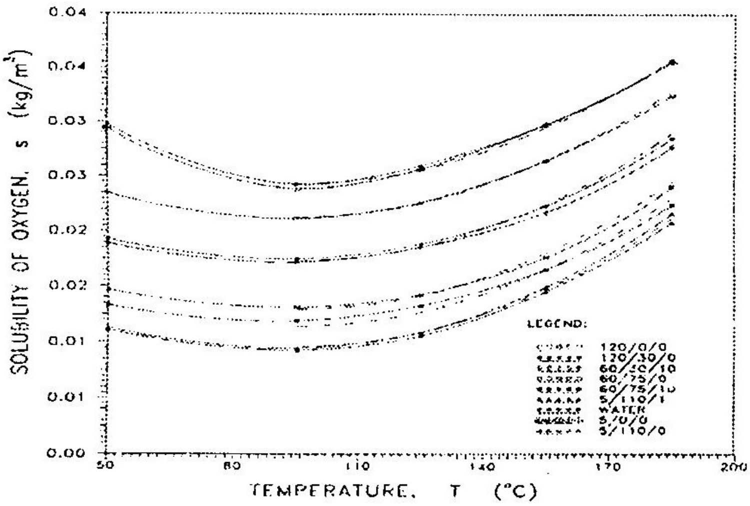


Fig. 4: **Oxygen solubility expressed in kg/m3 for a partial pressure of 101.3 kN/m2**

This is known to be true to a fraction of a percent for conditions used in these measurements[1,13]. In calculation of the solubility in kg/m3, it is necessary to know the number of moles of acid and dissolved salts per litre of solution, as well as the solution density at each temperature. The total number of moles were calculated and the densities were measured and are presented in Appendix A. The Bunsen coefficient, (ß), is sometimes used as well as Henry's constant (H) to describe the effect of pressure on gas solubility. Like the Henry's constant (H), the Bunsen coefficient (ß), representing the volume of gas at STP dissolved in a unit volume of solvent, is also constant with changing equilibrium pressure.

The error of the solubility results was estimated using the same computer programe applied in calculating other parameters. Solubility determinations using absorption methods alone may contain errors of up to 2%. When pure oxygen was used two consecutive operations are required for each determination; first, the absorption step at high pressure, and next, the desorption step at low pressure. The magnitude of error evaluated for the second step was 2% as well. In consequence, the overall error for most of the solubility results is estimated to be ± 4%. Finally for the results involving the solubility of oxygen from air, yet a third step was involved, and that was an analysis by GC of the desorbed gas at atmospheric pressure from the solutions saturated at higher pressures and temperatures. The uncertainty of the sampling and analysis procedure was also estimated at 2%. Thus, the overall uncertainty of the results involving the solubility of oxygen from air is estimated to be ± 6%.

Models for Oxygen Solubility in Synthetic Pressure Leaching Solutions

Approximate equations can be used to represent the oxygen solubility data in water and the solutions used. From Figs. 3 and 4, it is apparent that the nature of the temperature effect on solubility in the temperature range from 368 to 458 K is basically parabolic. Not as apparent is the linear effect of increasing the quantities of sulphuric acid, as well as of the dissolved zinc and iron sulphates in reducing the oxygen solubilities by an amount proportional to the concentrations. These effects are indicated in Fig. 5 which shows that the increase in concentrations of sulphuric acid reduced the oxygen solubility in direct proportion to the acid concentration, albeit a relatively small amount. The effect of increase in concentrations of dissolved zinc is much greater than that of sulphuric acid. A large reduction in solubility is observed with 110 kg/m^3 of zinc in solution, for example. Similarly, although not investigated in detail, there is a further reduction in the solubility as dissolved iron is added to the solution. Fig. 5 is typical of the solubility behaviour at the three other temperatures. It is also of considerable interest that quite closely, the effect of added acid, zinc or iron appear to be approximately the same at 368 K as at 428 and 458 K.

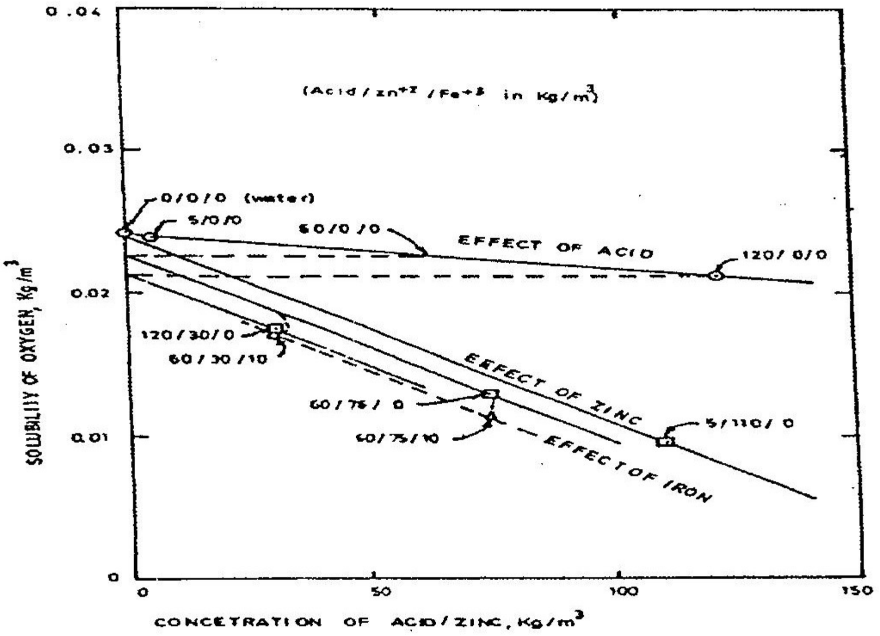


Fig. 5: **Effect of sulphuric acid, dissolved zinc and iron on oxygen solubility at 368 K**

Thus, it was possible to describe all solubility data by a model with the oxygen solubility (s) and concentrations of acid, zinc and iron (C_A, C_Z, C_I) all expressed in kg/m^3.

For water alone, the parabolic equation is:

$$S = 0.0244 + 0.144 \times 10^{-5} (T-95)^2 \qquad (1)$$

For aqueous acid, a decrement proportional to acid concentration is introduced:

$$S = 0.0244 + [0.144 (T-95)^2 - 2.60C_A] \times 10^{-5} \qquad (2)$$

For solutions containing dissolved acid, zinc and iron, further decrements are made:

$$S = 0.0244 + [0.144 (T-95)^2 - 2.60C_A - 13.2C_z - 15.0C_I] \times 10^{-5} \qquad (3)$$

The above equations were developed using a modelling procedure based on the data available and are only approximate because of the range of variables represented. The average absolute deviation of any one value from the measured solubility results of the synthetic solutions is 1.5%; with deviations as high as 3% in some instances. However, considering the amount of data represented by equation (3), the equation can be considered to be very successful indeed. Also, it can be stated that there is a systematic effect of the dissolved salts on the oxygen solubility in these solutions. The dashed lines in Fig. 4 indicate values calculated using equation (3) which can be compared with the experimental results represented by the solid lines. Equation (3) is valid for the temperature range of 368 K to 458 K, and concentration range 0 to 120 kg/m^3 acid, 0 to 110 kg/^{3} of dissolved zinc or 0 to 10 kg/m^3 of dissolved iron. It is a suitable model for interpolation of the solubilities at various temperatures and concentrations within the specified ranges.

Oxygen Solubility in Cominco Autoclave effluent and in a Sample Containing Lignosol

The results of the oxygen solubility for a zinc-rich solution containing 0.3 kg/m^3 lignosol (5/110/1/0.3) at 398 K using partial pressures of pure oxygen of 1013, 709.3 and 405.3 kN/m^2 indicate that the solubilities agree with Henry's law. This is the same result as that obtained for the other solubility determination with pure oxygen. Furthermore, the solubility of oxygen in the solution containing lignosol is essentially identical with that without lignosol (5/110/1) to within a fraction of a percent; as can be noted in Tables I and II. It should be mentioned that as part of the experimental procedure, the high pressure absorber was equilibrated for over 12 hours at high temperatures so that if lignosol tended to decompose, the equilibrium was with the lignosol decomposition products in solution. It appears that while the lignosol decomposition products may have useful surfactant properties, they do not significantly influence the oxygen solubility.

Table 2: **Oxygen solubility in an acid leach solution containing lignosol and a cominco pressure leaching autoclave effluent sample.**

		Temperature, K		
Composition		323	398	428
	s	-	0.0107	-
5/110/1/0.3	$(10^5)x$	-	0.624	-
(with oxygen)	$(10^{-3})H$	-	160	-
	ß	-	0.00745	-
	s	-	-	0.0143
5/110/1/0.3	$(10^{-5})x$	-	-	0.862
(with air)	$(10^{-3})H$	-	-	116
	ß	-	-	0.0063
	s	0.0073	-	-
Cominco Sample	$(10^5)x$	0.42	-	-
(with oxygen)	$(10^{-3})H$	238	-	-
	ß	0.0051	-	-
	s	-	-	0.0101
Cominco Sample	$(10^5)x$	-	-	0.627
(with air)	$(10^{-3})H$	-	-	159
	ß		-	-
		0.0076		

Note: Composition is in kg/m^3 of : acid/zinc/iron/lignosol, respectively.

The results for the solution containing lignosol (5/110/1/0.3) at temperature of 428 K using air at a partial pressure of air of 1013, 709.3 and 405.3 kN/m^2 indicate that Henry's law was obeyed and that only a slightly lower (by 2%) oxygen solubility was obtained with air than that obtained with pure oxygen, both calculated for the oxygen partial pressure of 101.3 kN/m^2. The result obtained with compressed air is 0.862 x 10^{-5} mole fraction oxygen compared with 0.880 x 10^{-5} for the comparable sample containing no lignosol and using pure oxygen. The reduction is 2.0% which is within experimental error. Thus, it may be concluded that lignosol has a negligible effect on the solubility of either pure oxygen or oxygen from air when added at a concentration of 0.3 kg/m^3.

The Cominco autoclave effluent sample of May, 1990, contained salts other than zinc and iron and hence, the oxygen solubility results cannot be compared with those for the prepared solutions. It was noted, however, that the density of the sample was significantly higher than that of all the synthetic solutions due to the higher concentrations of the dissolved salts (Appendices A and B). There was an inverse relationship between the density of the solution, which is affected by the concentration of the dissolved salts, and the oxygen solubility in it. The more dense was the solution, the lower was the solubility. Hence, it appears consistent that the high density plant solutions have a relatively low solvating power for oxygen. The results of the solubility obtained with pure oxygen at 101.3 kN/m^2 and temperature of 323 K and also compressed air at 428 K are listed in Table 2. It can be concluded that the low oxygen solubility in the plant solution has a profound effect on the oxidation rates of minerals present in the autoclave during pressure leaching.

The model for the oxygen solubility was tested with the Cominco plant sample even though the concentration of zinc in this sample exceeded that for which the equations are applicable. It was assumed that magnesium had the same influence on the solubility as zinc. Then, the oxygen solubility corresponding to a partial pressure of 101.3 kN/m^2 is 0.0076 kg/m^3 compared to the measured solubility of 0.0101 kg/m^3. On the other hand, if the effects of magnesium, copper and calcium are neglected, the calculated solubility is 0.0088 kg/m^3, a difference of 13% from the measured solubility. Although these models give correct order-of-magnitude results, it should be expected that they cannot give accurate prediction of the Cominco plant sample behaviour.

CONCLUSIONS

i The oxygen solubility in aqueous solutions of sulphuric acid and zinc and iron sulphates is very low. For an oxygen partial pressure of 101.3 kN/m^2 the solubility is in the order of 0.02 kg/m^3 or 1×10^{-5} mole fraction oxygen.

ii The solubilities of oxygen in aqueous sulphuric acid containing zinc and iron sulphates conform with Henry's law.

iii There is a minimum solubility of oxygen in water and in aqueous solutions of sulphuric acid and zinc and iron sulphates at a temperature of about 368 K.

iv There is a proportional decrease in oxygen solubility with increase of content of zinc and/or iron and/or acid in the solution.

v The two-stage process can be successfully utilized to measure the solubilities of oxygen in aqueous solutions; first, by batchwise saturation at high pressure and then by quantitative desorption and expansion of the gas through a needle valve at low pressure using a flow process.

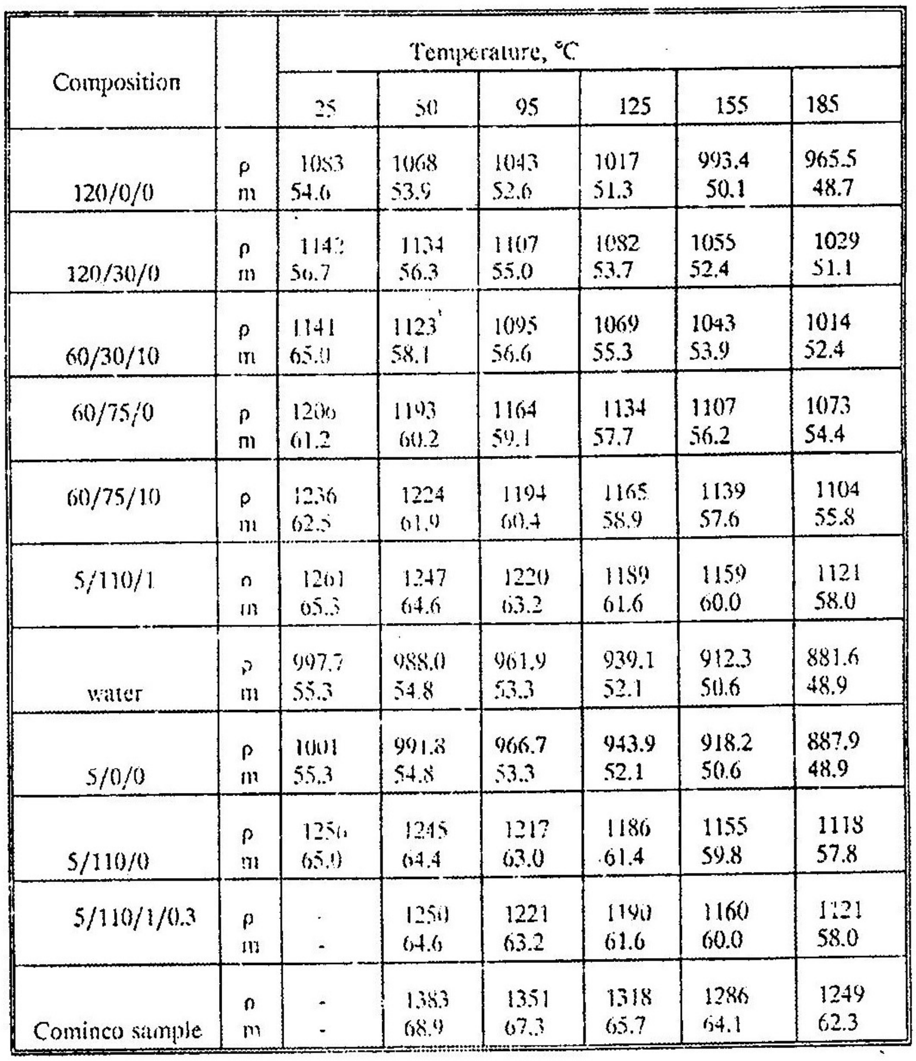
REFERENCES

1. R. Battino, "IUPAC Solubility Data Series; Oxygen and Ozone," Vol. 7, Pergamon Press, Headington Hill Hall, (1981).
2. E.L. Stephan, N.S. Hatfield, R.S. Peoples and H.A.H. Pray, Battelle Memorial Institute report BMI-1067", (1956).
3. A.V. Klyueva, "Tr. Ural. Poltekh. Inst., No 155, 39-44, (1967).
4. V.R. Choudhary, M.G. Parande and P.H. Brahme, "Simple Apparatus for Measuring Solubility of Gases at High Pressures", *Ind. Eng. Chem. Fundam.*, **21**, (1982), pp. 472-474
5. T.J. Morrison and F. Billet, *J. Chem. Soc.*, 2033, (1948).
6. W. Hayduk, and S.C. Cheng, "Solubilities of Ethane and Other Gases in Normal Paraffin Solvents", *Can. J. Chem. Eng.* **48**, (1970), p. 93
7. W. Hayduk, and H. Laudie, "Solubilities of Gases in Water and Other Associating Solvents", *AIChE Journal*, **19**, (1973), p. 1233.
8. J.M. Prausnitz, and R.N. Lichtenthaler, "Molecular Theory of Fluid Phase Equilibria", 2nd ed., Prentice Hall, Eaglewood Cliff, (1986).
9. D. Beutier, and H. Renon, "Gas Solubilities Near the Solvent Critical Ponit", *AIChE Journal,* **24**, (1978), p. 1122.
10. W. Schotte, "Solubilities Near the Solvent Critical Point", *AIChE Journal,* 31, (1985), p. 154.
11. M.L. Japas, and J.M.H.L. Sengers, "Gas Solubility and Henry's Law Near the Solvents Critical Point",
12. A.M. Harvey, and J.M.H.L. Sengers, "Correlation of Aqueous Henry's Constants from 0°C to the Critical Point", *AIChE Jour-*

nal, **36,** (1990), p.546.
13. R.C. Weast, "CRC Handbook of Chemistry and Physics", 70th ed., CRC Press, Boca Raton (1989).

Appendix A

Table 3 Densities and molar concentrations for test solutions



Composition		Temperature, °C					
		25	50	95	125	155	185
120/0/0	ρ	1083	1068	1043	1017	993.4	965.5
	m	54.6	53.9	52.6	51.3	50.1	48.7
120/30/0	ρ	1142	1134	1107	1082	1055	1029
	m	56.7	56.3	55.0	53.7	52.4	51.1
60/30/10	ρ	1141	1123	1095	1069	1043	1014
	m	65.0	58.1	56.6	55.3	53.9	52.4
60/75/0	ρ	1206	1193	1164	1134	1107	1073
	m	61.2	60.2	59.1	57.7	56.2	54.4
60/75/10	ρ	1236	1224	1194	1165	1139	1104
	m	62.5	61.9	60.4	58.9	57.6	55.8
5/110/1	ρ	1261	1247	1220	1189	1159	1121
	m	65.3	64.6	63.2	61.6	60.0	58.0
water	ρ	997.7	988.0	961.9	939.1	912.3	881.6
	m	55.3	54.8	53.3	52.1	50.6	48.9
5/0/0	ρ	1001	991.8	966.7	943.9	918.2	887.9
	m	55.3	54.8	53.3	52.1	50.6	48.9
5/110/0	ρ	1256	1245	1217	1186	1155	1118
	m	65.0	64.4	63.0	61.4	59.8	57.8
5/110/1/0.3	ρ	-	1250	1221	1190	1160	1121
	m	-	64.6	63.2	61.6	60.0	58.0
Cominco sample	ρ	-	1383	1351	1318	1286	1249
	m	-	68.9	67.3	65.7	64.1	62.3

Note: ρ = density, kg/m^3
m = molar concentration, kmol/m^3

Note: p = density, kg/m3
m = molar concentration, kmol/m3

Appendix B

Analysis of Cominco Autoclave effluent sample (analysis as determined by Cominco laboratory).

Date: May 28, 1990

Source of sample: Cominco autoclave effluent, after 6-8% water loss because of flashing during sampling.

Components and concentration:

Zinc	145 g/l
Iron $^{2+}$	5.9 g/l
Free acid	32.3 g/l
Magnesium	9.1 g/l
Lignosol	0.6 g/l (0.3 g/kg)
Calcium	380 mg/l
Copper	935 mg/l

Normal additional components not specified in the assay:

Manganese	1.5 to 2.0 g/l
Cadmium	0.5 g/l

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