The Development of Mode for Solubility of Oxygen in High Pressure Condition

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Abstract. Previous investigation of solubility of oxygen in high pressure is summarized in the paper. Summing-up shows that compared with various methods for such measurement, solubility theory is developed slowly. Models for prediction of oxygen solubility in aqueous acid and/or salt solution have been developed. However, no model can reproduce the existing experimental data, and extrapolate beyond the data range from simple aqueous salt system to complicated brine systems including seawater, simultaneously. A model to cover much wider temperature and pressure space in variable composition brine systems needs much more efforts. At last, the main consensuses and differences as well as the further work is reviewed.

1. Introduction
Oxygen leaching is an important hydrometallurgical process that is frequently considered for the pretreatment and upgrading of ores at elevated temperatures and pressures. The solubility of oxygen in the aqueous phase determines the availability of oxidant during leaching and, in the case of high operating temperatures, the volume of oxygen that is evolved during cooling of the leached solution. A detailed knowledge of temperature and pressure effects on oxygen solubility enables the leaching processes to be modeled and controlled more effectively[1-2].

2. Mode for Theories
Some authors suggested some methods or models for predicting the effect of ions (or salts) on the gas solubility. Two models (the setschenow salt effect parameter and the ionic strength effect) are introduced for this purpose.
2.1. Mode 1: The Setschenow Salt Effect Parameter

Studies concerning the effect of dissolved salts on gas solubility are well presented by Ting Gong et al.[3]. The magnitude of the effect of salts on the activity coefficient of a dissolved gas in aqueous solution 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:

\[ \log \gamma_B = k_s C_s + k_B C_B \]  

(1)

In Expression (1), \( \gamma_B \) is the salt effect parameter, \( k_s \) is the solute-solute gas interaction parameter. It is considered that dissolved gas activity in the pure solvent is same as that in the solution.

\[ \alpha_B = \gamma_B^0 S_B = \gamma_B^0 S_B^0 \]  

(2)

In Eq. (2), \( r_B \) and \( S_B \) are in the solution, \( r_B^0 \) and \( S_B^0 \) in the pure solvent. Also, and are their corresponding activity coefficients. Therefore, the following equation results:

\[ \log \frac{\gamma_B^0}{\gamma_B} = \log \frac{S_B^0}{S_B} = k_s C_s + k_B (C_B - C_B^0) \]  

(3)

If the gas solubility is low, the term with can be neglected, thus:

\[ \log \frac{\gamma_B^0}{\gamma_B} = \log \frac{S_B^0}{S_B} = k_s C_s \]  

(4)

The Setschenow salt effect parameter, \( k_{SCA} \), is defined as follows:

\[ k_{SCA} = \frac{1}{C_R} \log \left( \frac{S_B^0}{S_B} \right) \]  

(5)

In Eq. (5), \( C_R \) is the total electrolyte concentration.

The salt that increase the activity coefficient of the dissolved gas is said to “salt out” the gas and the salt that decrease 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 solubility of gases in water is 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. Mode 2: The Effect of Ionic Strength

Based on the Setschenow salt effect parameter, Braibanti et al [4] proposed a method to estimate the solubility in electrolyte solutions. In this method, the Henry’s law constant in the solution in the solution is related to that in water at the same temperature as shown in the following expression:

\[ \log \frac{K_B}{K_B^0} = \log \frac{S_B^0}{S_B} = h_1 I_1 + h_2 I_2 \]  

(6)

In Eq. (6), \( I_1 \) is the ionic strength of the solution defined by:

\[ I_1 = \frac{1}{2} C_i (Z_i^2 + Z) \]  

(7)

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

\[ h = h_1 + h_2 + h_G \]  

(8)
In Expression (8), \( h_+ \), \( h_- \), and \( h_G \) are the contribution 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 the parameter \( (h_+ , h_- , \text{ and } h_G) \) in the model are independent of the composition of aqueous salt solution.

3. Mode for Experiments

3.1. Mode 1: In Pure Water

The solubility of oxygen in water is known precisely. The work is considered to be the most precise measurement of gas solubility to date. They have proposed an equation to predict the amount of oxygen dissolved in water, in the temperature range from 273.15 k to 373.15 k, with a standard deviation of 0.017%. For that reason, the solubility of oxygen of oxygen in water can serve as a reference to ensure the reliability of the solubility apparatus, and more importantly, the experimental technique of the investigator. After examination of the water reference system, gas solubility in sulfuric acid and copper sulfate solutions were measured[5].

3.2. Mode 2: In Sulphuric Acid/Or Salt Solution

Qin Li et al[6] investigated the solubility of oxygen in sulfuric acid solutions containing cupric and/or nickel sulfate at atmospheric and high pressures, and found that the logarithm of oxygen solubility in aqueous acid-salt solution is lineally 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 more advantages, compared with the models proposed by Tan et al[7]. The effects of temperature and pressure on oxygen solubility are also discussed. In the solutions studied, the oxygen solubility as a function of temperature follows a similar pattern to that in water. For different pressures, Henry’s law is obeyed in the range of this research (<5 atm). Very few workers have measures the solubility of oxygen in aqueous sulfuric acid solutions. Those who did, did not cover sufficient common ranges of concentration and temperature for direct comparison. The data available are thus, considered tentative only.

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

At a given temperature and partial pressure of oxygen, the solubility decreases with an increase in the sulfuric acid concentration. The solubility increases with the increase in the partial pressure of oxygen at a constant temperature and concentration. As expected, the gas solubility increased with the increase in partial pressure of oxygen at a constant temperature as expressed by Henry’s law.

A complication of oxygen solubility in various aqueous solutions was produced in 1981 by Battino et al. surprisingly, only six reports concerning the solubility of oxygen in aqueous sulfuric acid solution were found. Most of his initial work was performed near the turn of the century. Additional data were made by Frank et al.[8], at five temperatures between 323 and 523 k and for concentrations of 0.5, 1.0, and 1.5 mol/l sulfuric acid solutions, show a decrease in the solubility from 323 to 373 k. this is followed by an increase from 373 to 723, 473 and to 523 k. thus, a minimum solubility was indicated at 373 k.

Gubblins and Walker measured the solubility of oxygen in sulfuric acid solutions at higher concentrations of the acid. The results indicated that oxygen solubility decreases to a minimum at about 80% by mass H\(_2\)SO\(_4\) is approached.

Shimizu et al[9] is the only person who measured the solubility of oxygen in aqueous sulfuric acid solutions containing salts. He measured the solubility at oxygen partial pressure of 0.25 and 1.0 MPa (2.5 and 10 atm) at six temperatures between 323 and 473 k. the concentration of the solution was
0.0125 mol/l sulfuric acid and saturated with either nickel sulfide (NiS$_2$), copper sulfide (Cu$_2$S) or cobalt sulfide (Co$_4$S$_3$). The actual sulfide concentrations were not given. The sulfuric acid-metal sulfide decreased the oxygen solubility to less than 50 percent its solubility in water. The variation of oxygen solubility with temperature and partial pressure of oxygen followed the same trend as those plain sulfuric acid solutions.

Sinha et al[10] carried out a thermodynamic analysis of the temperature dependent equilibrium between oxygen solubility activity in pure water and oxygen partial pressure. He used experimental oxygen solubility sources to determine a set of self consistent values for the chemical potential, entropy and partial molar heat capacity of dissolved oxygen, then combine with established thermodynamic data for gaseous oxygen to develop a single thermodynamic equation describing the relationship between gaseous oxygen fugacity, dissolved oxygen activity, Temperature and the equilibrium constant $k$. This equation was consistent with $k$ values calculated from published experimental solubility data for temperatures from 273 to 616 K and pressures to 60 atm, encompassing the conditions encountered during oxygen leaching operations. Within these ranges, it was shown that the gas fugacity and dissolved oxygen activity coefficients were sufficiently close to unity that the $k$-equation may be used to relate the moral concentration of dissolved O$_2$ for any combination of temperature T(K) and (atm).

\[
C_{\text{aq}} = P_{\text{O}_2} \exp \left\{ \frac{0.0467 + 203.357 \ln \left( \frac{T}{298} \right) - (299.378 + 0.092T)(T - 298) - 20.591 \times 10^4}{(8.3144)T} \right\}
\]

(9)

4. Main Conclusions

Great numbers of data on solubility of oxygen in high pressure conditions have been measured, and some models have been built, the trend of change can be sure to predict. But a more accurate data and model need further investigation.

(1) The main consensuses and differences are as follows:

(a) The solubility of oxygen in water approaches a minimum at about 373.15 k. Oxygen solubility in aqueous sulfuric acid-salt sulfate solutions has a minimum solubility at a temperature of about 368 k.

(b) The aqueous solution did not closely obey Raoult’s law, hence the activity coefficient for the electrolytes were calculated from the vapor pressure data.

(c) The solubility of oxygen in the aqueous sulfuric acid-salt leach solutions closely obeys Henry’s law.

(d) As the temperature is increased from 368 k to 458 k, there is generally a large increase in the solubility of oxygen in the aqueous sulfuric acid-salt leach solution.

(e) In a given temperature and pressure ranges, the densities of the solutions decrease as the temperature is increased following the same pattern as that for pure water, and increase with an increase in concentration of iron, zinc and/ or sulfuric acid.

The main difference is that some workers state that the salt out of oxygen from the aqueous solutions was found to be function of the type of electrolyte added. However, the Setschenow salt effect parameter, for a given electrolyte, was found to decrease slightly as the concentration of the electrolyte was increased., but some insist that marked reduction in the oxygen solubility is observed at all temperatures as the quantity of dissolved zinc sulfate is increased in the solution.

(2) The further work

(a) A more universal model is to be developed for more accurate predict solubility of oxygen in different media and (or) condition.

(b) A detail method and program is to be made to fully automate measurement of solubility of oxygen for the chemical industry and metallurgical industry.

(c) Parameters about solubility of oxygen such as activity should be measure accurate to better model building.
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