

Gas solubilities in molten salts and silicates

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Abstract—Solubility phenomena of some gases in typical salt and silicate melts are surveyed. Chemical absorption involves solute-solvent interactions, and the acid-base concept, among others seems to be effective in the understanding of solubility. Solubilities of carbon dioxide, water and cyanide ion are discussed as the examples.

INTRODUCTION

The solubility phenomena of various gases in high temperature melts can be classified into two groups; i.e. physical and chemical. The former is represented by noble gases dissolved in typical halide salts. The solubility is interpreted by Ulig-Blander theory in which the gas molecule is considered to create a cavity whose surface energy is related to the thermodynamic surface tension of the solvent. Thus, the solubility increases with temperature. The review article by P. Field (ref. 1) gives a comprehensive view of the physical solubility in typical molten salts.

The present author wishes to draw attention to the chemical absorption associated with exothermic effect. Gaseous solute chemically interacts with solvent molecules. As will be seen later, acid-base character of solvent molecules becomes important, although gas absorption is sometimes accompanied by redox reactions involving solute and solvent molecules.

The experimental techniques will be described first, with particular attention being given to devices specific to high temperature melts. Next the solubilities of CO_2 , H_2O , CN^- in salts and oxide slags are discussed in relation to the nature of solvents. The articles quoted in this communication were selected according to the authors interest and the review is not intended to survey all the references related to the present subject.

SOLUBILITY MEASUREMENTS

Gas solubility is usually low and Henry's law is obeyed. Therefore, experimental works are essentially the determination of Henry's law constant K_H defined as

$$P_2 = K_H X_2 \quad (1)$$

where P_2 and X_2 are pressure and mole fraction of the solute in the salt melt respectively. Another equilibrium constant defined as

$$K_P = C_2/P_2 \quad (2)$$

is also employed, where C_2 is the concentration. $\ln K_H$ and $\ln K_P$ and their temperature dependences lead to the important thermodynamic quantities of gas absorption. A gas molecule may dissociate into two or more components in the melt. Then eq(1) does not hold any more since P_2 becomes proportional to the square or higher power of the concentration.

The principles of experimental methods adopted at high temperature melts are the same as those employed at room temperature. However, the attainment of equilibrium, the handling of solvent melts and the concentration analysis' technique may require extra cautions. The experimental methods can be categorized into three classes:

(1) Absorption measurements by volumetric, manometric or gravimetric devices. Hygroscopic reactivity and high vapor pressure of solvents require a special device for solvent preparation and introduction to the measuring system. This typical device has been well described by Borodzinski et al. (ref. 2). Analysis of the glass sample quenched after equilibration has also been done (ref. 3). The drawback of this method is its slow attainment of equilibrium. With oxide melts it takes quite a long time (72hr for CO_2 in a silicate).

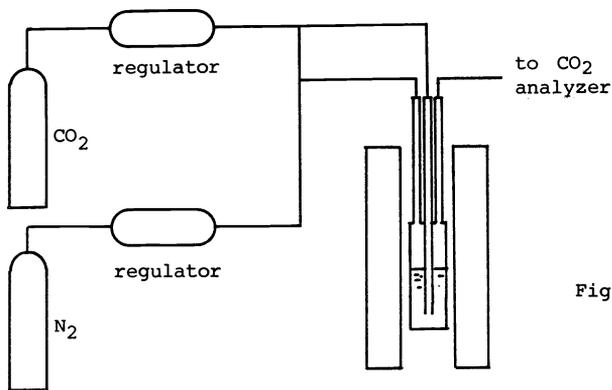


Fig. 1. Schematic sketch of elution method

(2) Elution from saturated melts. This is adequate for high temperature melt. A schematic diagram of that system (ref. 4) is shown in Fig. 1.

(3) A third somewhat limited method is cryometry, where the freezing point depression due to the gas absorption is measured. The reader is advised to consult another review paper by Flengas and Block-Bolten (ref. 5) for various experimental methods and solubility data. One experimental arrangement may not cover a wide temperature range. This results in an unsatisfactory heat of solution.

INTERESTING EXAMPLES

Carbon dioxide in molten salts

Solubility of carbon dioxide in molten salts have been extensively measured from both the physical and chemical view points. However, the solubility even in typical halide salts has not been well interpreted.

Here, the solubility in relation to the solvent basicity will be taken up. Carbon dioxide is a weak acid and responds to the basicity of the solvent. In a long series of works, Tremillon and coworkers have developed the electrochemical measurements of redox as well as acid-base reaction in molten salts. They measured the equilibrium carbon dioxide pressure as a function of either carbonate or hydroxide ion contents in lithium-potassium chloride eutectic mixtures (ref. 6).

A stabilized zirconia membrane electrode was immersed in the solvent melt in order to monitor the O^{2-} concentration and they confirmed the following reaction



to be at equilibrium. Fig. 2 shows an example of the results. Oxide ion was found to be generated by dissociation of added carbonate. Reversibly, hydroxide determines the

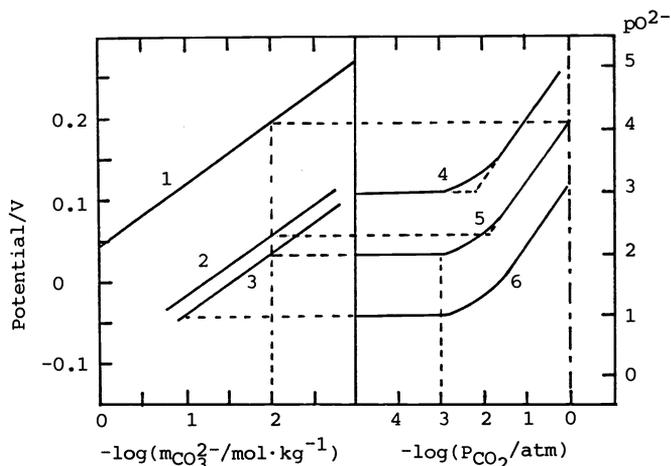


Fig. 2. Potential of stabilized zirconia membrane electrode with the equilibrium eq. (3)

1 to 3: potential vs molality of Na_2CO_3 under 1 atm, 10^{-2} atm, and $< 10^{-3}$ atm CO_2 respectively

4 to 6: potential vs CO_2 pressure at molality of Na_2CO_3 , 10^{-3} , 10^{-2} , and 0.1 mol/kg respectively.

solubility of carbon dioxide. Its solubility can also be controlled by HCl/H₂O gas mixture as follows



Nitrogen monoxide and dioxide solubilities in sodium nitrate-nitrite mixture were also determined by Tremillon et al. as functions of either oxygen pressure or $p\text{O}^{2-}$ ($\equiv -\log[\text{O}^{2-}]$) (ref. 7). The relevant chemical reactions were as follows



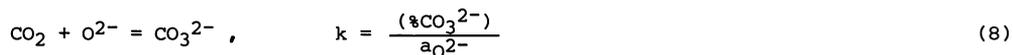
It is interesting to note that CO₂ responds to O²⁻ exclusively, inspite of the fact that the chloride ion is regarded as a base, though a weak one.

Carbon dioxide in molten silicate

Among many studies on carbon dioxide solubility in silicate melts, Pearce's data (ref. 3) are of special value, since he tried hard to establish the equilibrium in viscous melts at high temperatures. He measured the solubility over a composition range of 25 to 56 wt% Na₂O at temperature range of 900 to 1400°C.

When the sample melts were equilibrated with 1 atmospheric carbon dioxide, they were quenched and analysed by a vacuum-fusion apparatus.

He treated the data by the equilibrium,



His results showed that the basicity changed as much as 4 orders of magnitude when sodium oxide content increased from 25 to 55 %. Fig. 3 shows the carbonate content as function of sodium oxide in the solvent as well as the thermodynamic activity of sodium oxide of the sodium oxide-silica solvent measured later by us (ref. 8), as designated as $p\text{O}$. This is similar to $p\text{O}^{2-}$ measured in molten salts. Except for the arbitrary unit of the vertical axis, a steep increase of carbonate solubility is shown to coincide with increase of sodium oxide activity (decrease of $p\text{O}$).

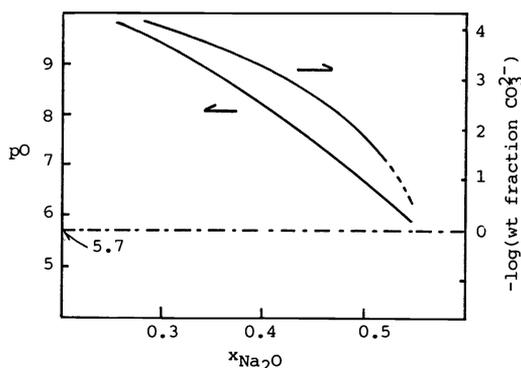
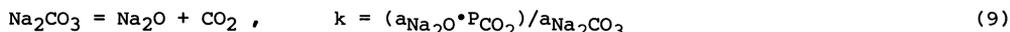


Fig. 3. Basicity $p\text{O}$ and carbonate solubility as functions of the composition of sodium oxide-silica melts

$$p\text{O} \equiv -\log(\text{activity of Na}_2\text{O})$$

$$x_{\text{Na}_2\text{O}} \equiv \text{mole fraction of Na}_2\text{O}$$

In order to understand the situation, let us consider the thermal decomposition of sodium carbonate



The free energy data lead us to $k = 10^{-5.7}$ at 1300 K. In other words, the activity of sodium oxide is $10^{-5.7}$ when sodium carbonate is in equilibrium with one atmospheric carbon dioxide. The corresponding k for the decomposition of the silicate melt of equimolar ratio,



is $10^{-6.5}$. The important consequences of this data are as follows;

- (1) Carbon dioxide is not so weak an acid compared with SiO₂ as we may imagine.
- (2) When the activity of Na₂O decreases below $10^{-5.7}$ by addition of acid oxide in the slag, carbon dioxide, if ever dissolved, starts to effervesce. In other words, any stronger acid can displace carbon dioxide in the slag.
- (3) In the presence of carbon dioxide gas, sodium oxide activity never exceeds $10^{-5.7}$.

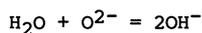
Along with (2) soda ash is a mild base and yet highly capable of functioning as a base since the acid component (carbon dioxide) is easily driven to the gas phase.

Water in silicate melts

Water vapor is another important substance as a gaseous solute. Elimination of water from glass is quite important step since water causes gas bubbling as well as IR absorption. The metallurgical slag must also be dried up otherwise it can affect the hydrogen content in steel. Fig. 4 is a diagram taken from the work by Fukushima et al. (ref. 9) showing solubility as a function of water vapor pressure. The square root dependence means dissociation of the water molecule into two particles. The composition dependence is shown in Fig. 5 (ref. 9). The solubility is high at both acidic and basic sides and much less at the intermediate. Figs. 4 and 5 demonstrate the process of absorption to be



in the acidic range, and



in the basic.

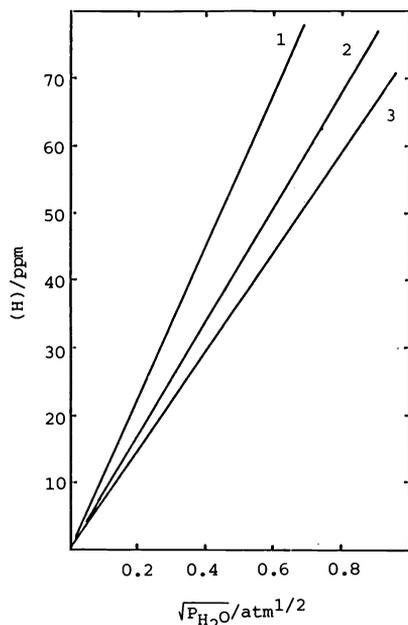


Fig. 4. Hydrogen content vs pressure of water vapor

- 1: a basic open hearth slag at 1550°C
- 2: 40CaO•40SiO₂•20Al₂O₃ at 1550°C
- 3: 15Na₂O•25CaO•60SiO₂ at 1300°C

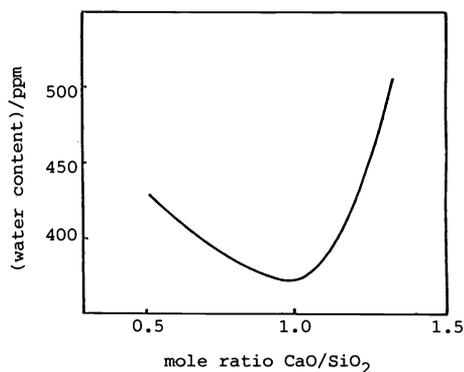
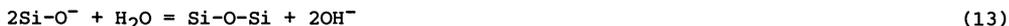


Fig. 5. Solubility of water vs mole fraction ratio of CaO to SiO₂ in CaO-SiO₂ melt at 1600°C.

Thus, water functions as a base in eq(11) and as an acid in eq(12), in the sense defined by Lux (ref. 10) and Flood and Forland (ref. 11).

Ref. 10's authors proposed also the following two reactions



which might proceed in a weak basic range. Considering the standard free energy change, both reactions do not contribute much. This may be the reason why the solubility is low at intermediate range. Figs. 6 and 7 (ref. 12) show the effect of other oxides at different calcium oxide silica ratios. The tendencies can be understood from acid-base bases. Thus, in the basic solution (Fig. 6) acidic oxides diminish the solubility, while in an acidic range (Fig. 7) acidic oxides enhance it. Alumina shows a peculiar effect.

Cyanide ion in oxide melts

Chemical solubility of nitrogen in oxide melts in reducing atmosphere have been known in glass industry as well as metallurgy. Esin and his coworkers seem to be the first in the identification of the chemical species. When they used graphite crucible as the container, they proposed solubility to be proportional to $P_{\text{N}}^{1/2} P_{\text{CO}}^{-1/4}$ (ref. 14) and $P_{\text{N}}^{1/2} P_{\text{CO}}^{-1}$ (ref. 14). Evolution of silicon monoxide gas prevents this study in wide silica content range. Alumina increases the solubility. The recent investigations (refs. 15, 16) conclude that nitrogen dissolves as nitride and cyanide ions, while carbon dissolves as carbide ions (C^{4-} and C_2^{2-}) plus cyanide ion,



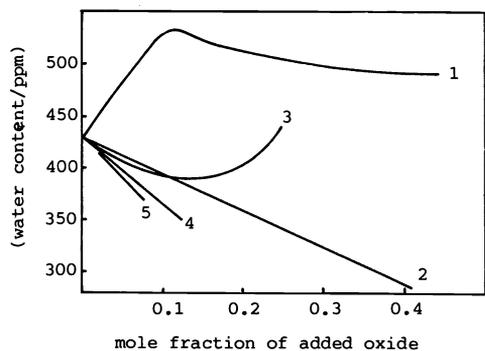


Fig. 6. Solubility of water vs added oxides in CaO-SiO₂ melt of CaO/SiO₂ = 1.3 at 1550°C and P_{H₂O} = 289 Torr.

Curve nos. in Figs. 6 & 7:

- 1: AlO_{1.5}
- 2: TiO₂
- 3: BO_{1.5}
- 4: PO_{2.5}
- 5: GeO₂

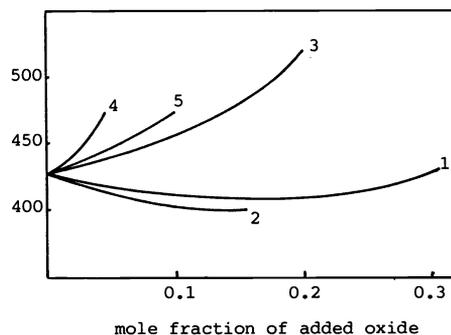


Fig. 7. Solubility of water vs added oxides in CaO-SiO₂ melt of CaO/SiO₂ = 0.63 at 1500°C and P_{H₂O} = 289 Torr.

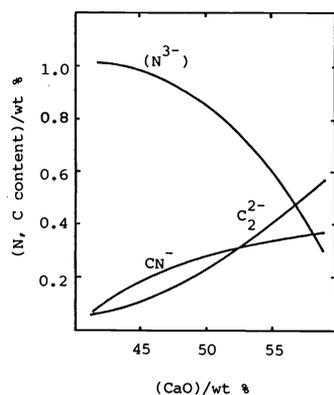


Fig. 8. Contents of three species vs CaO content in CaO-Al₂O₃ melt at 1550°C, P_{N₂} = 0.92 atm, and P_{CO} = 0.08 atm (ref. 16).

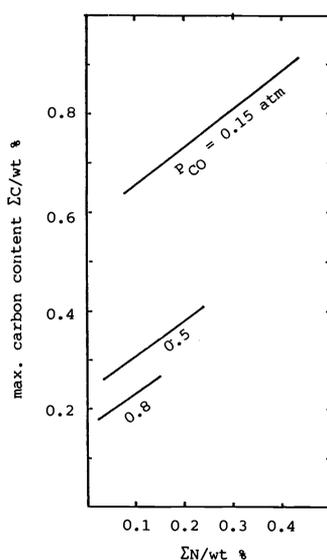


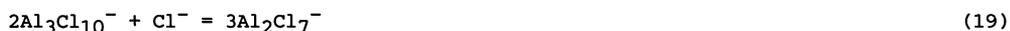
Fig. 9. Maximum (ΣC) content vs (ΣN) content in 45 wt % Al₂O₃ 55 wt % CaO binary melt in graphite crucible at 1600°C at three CO pressures.

Addition of CaF₂ enhances nitrogen solubility (ref. 17). Figs. 8 and 9 show the results of the two groups.

BASICITY OF SOLVENT MELTS

As is shown above, the so-called basicity of solvents plays the decisive role in determining the chemical solubility of gases. Alternatively, the solubility of a gas gives a good measure of the solvent basicity.

The acid-base concept of halide melts is itself well represented by NaCl-AlCl₃ system. Thus, the equilibrium pressure of aluminum chloride above the melt is interpreted by assuming a series of reactions, (ref. 18)



Here, Cl⁻ is a Lewis base and its activity-derived function pCl = -log[Cl⁻] determines the thermodynamic state of the chloride mixture. The basicity of oxide melts is similarly defined. We (ref. 8) have measured the basicity of various binary oxide melts where sodium oxide is the common basic component. Since no other supporting electrolyte is present, we were forced to employ the activity of sodium oxide rather than that of oxide ion to express the thermodynamically sound basicity. As described in the preceding section, the sodium oxide activity is in qualitative agreement with the carbon dioxide solubility. If the carbonate content is kept low by lowering the carbon dioxide partial pressure, its solubility would show a much better agreement with the activity.

It would be interesting to recall the paper by Angell (ref. 19). He showed the similarity between the following two reactions,



where an aqueous solution of pH 14 rather than of 0 was considered to be the reference. He looked from the viewpoint that various oxides dissolve into a similar species in both solvents and their redox potentials line up in an analogous order. His point is quite important since we are likely to consider an acid solution of pH 0 in such a case.

Now, let us consider oxide-halide anionic mixtures. Why do we not have a common basicity scale? The question is concerned with the definition and the measurement of the basicity. In the field of metallurgy, carbon dioxide solubility was recommended as the measure. However, this measurement seems not to cover halide solvents. The optical basicity proposed firstly by Duffy and Ingram (ref. 20) hopefully seems to meet this end. The principle of experimental method lies behind the fact that the energy of 6s-6p excitation of Tl^+ , Pb^{2+} , and Bi^{3+} probe ions depends on the electron donating tendency of the surrounding solvent atoms. The recent analysis (ref. 21) shows promise of generalization. However, as we go into the details of chemical interaction between the probe and the solvent atoms, the character of each probe as an acceptor of an electron pair becomes too complex to allow generalization. Semi-empirical quantum mechanical approaches have been undertaken (refs. 22, 23). For the metallurgical purpose, empirical parameters like sulphide and phosphate capacities are in practical use.

CONCLUDING REMARKS

Chemical solubilities of some gases in high temperature melts were briefly reviewed. Combination of liquid solvents with soluble gases provide media for various chemical reactions, where catalytic action of the solvent, separation by selective adsorption or slowing down the speed of otherwise explosive reaction and so on are put into practice.

Much studies on experimental measurement and theoretical attack are required to elucidate the details of solute-solvent interactions before the solubility of chemically active gases are fully understood. Measurement at high pressures will increasingly become important from the geological as well as industrial viewpoints. Extraordinary solvents like superacids, which have not been touched here, might become important for a particular gas.

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