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The Solubility of Sulfur in Na_2O-SiO_2 Melts under Various Oxygen Partial Pressures at 1100 °C, 1250 °C, and 1300 °C

Shigeru NAGASHIMA and Takashi KATSURA

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The solubility of sulfur in Na_2O–SiO_2 melts with the Na_2O/SiO_2 molar ratios of 1/3, 1/2, and 1/1 was investigated by varying the oxygen partial pressure at 1100, 1250, and 1300 °C. The results at 1100 °C are complicated, for the equilibrium state within the gas phase is not established. From the experiments at 1250 and 1300 °C, the following conclusions are reached: (1) When the temperature and the Na_2O/SiO_2 ratio in the melt are constant, the solubility of sulfur increases with an increase of the total amount of sulfur in the gas phase. (2) When the temperature, the Na_2O/SiO_2 ratio, and the total amount of sulfur in the gas phase are constant, the solubility of sulfur shows its minimum at a specific oxygen partial pressure; at higher oxygen partial pressures, the sulfur dissolves in the melts mostly as sulfate, while at lower oxygen partial pressures, the sulfur dissolves mostly as sulfide. (3) When the temperature and the total amount of sulfur in the gas phase are constant, the solubility rises greatly with an increase in the Na_2O/SiO_2 ratio in the melt. (4) When the Na_2O/SiO_2 ratio in the melt and the total amount of sulfur in the gas phase are constant, the minimum point of the solubility shifts in the direction of higher oxygen partial pressures as the temperature increases. This corresponds to the shifts of the equilibrated gas composition as the temperature increases.

The solubility of sulfur in melts at high temperatures is important not only for geochemistry but also for metallurgy and ceramics. Fincham and Richardson[1] investigated the effect of the oxygen partial pressure on the solubility of sulfur in silicate and alumino silicate melts by equilibrating the melts with gas mixtures (SO_2–CO_2–H_2) at 1350—1650 °C. On the basis of thermodynamic calculations at 1425—1650 °C, they concluded that sulfur dissolves in the CaO–Al_2O_3–SiO_2 melts as sulfate at oxygen partial pressures higher than about 10^{-3} atm, and that sulfur dissolves as sulfide at oxygen partial pressures lower than about 10^{-5} atm. Similar results were obtained later by other investigators[2–3] using different kinds of melts. However, no study has been published on the alkali silicate systems.

The present objectives are to: (1) obtain fundamental thermodynamic information about the solubility of sulfur in the Na_2O–SiO_2 melts and (2) actually prove the dissolving state of sulfur in silicate melts by chemical analysis. The solubility of sulfur was studied at very high oxygen partial pressures by Holmquist,[4] but no study has ever been made over wider range of oxygen partial pressures.

Experimental

Furnace, Temperature Control, and Procedure. These were almost the same as those adopted by Iwasaki and Katsura.[5]

Gas Mixture. Commercial gases (SO_2, CO_2, and H_2) were purified with phosphorus pentoxide and were mixed in the required ratio by a capillary technique. The rate of gas flow was fixed at 0.66 cm/s throughout the present experiments. Preliminary experiments at about 0.3 cm/s proved that the gas-flow rate does not have any significant effect on the results.

Materials. Sodium silicate glasses with the required compositions (the Na_2O/SiO_2 molar ratios of 1/1, 1/2, and 1/3) were prepared by melting mixtures of sodium carbonate and silica of an analytical grade in platinum crucibles. The sodium contents of these glasses were chemically analyzed in the form of Na_2SO_4 after dissolving the glasses with HF and H_2SO_4; the results agreed well with the calculated values within an error of 0.5%. The sulfur content of these glasses was less than 0.001%. Samples with a known amount of sulfur were also prepared by melting mixtures of sodium carbonate, sodium sulfate, and silica.

Chemical Analysis of Total Sulfur. The total sulfur in the quenched samples was determined by the following two methods, according to the sulfur content: (1) for high concentrations of sulfur (>0.5%), the sulfur was determined by the method of Kiba *et al.*[6] with some modifications; (2) for low concentrations of sulfur (0.001—0.5%), the sulfur was determined as in a previous paper.[7] In order to check the reliability of the methods, the sample with a known amount of sulfur mentioned above was analyzed by the methods, (1) and (2). Some results for the samples with the Na_2O/SiO_2 ratio of 1/2 were as follows: (Added: 4.0% S, Found: 3.9, 4.0, 3.7% S; Added: 0.34% S, Found: 0.32, 0.34, 0.33% S).

Chemical Analysis of Sulfide- and Sulfate-Sulfur. The sulfide- and sulfate-sulfur in the samples was determined with tin(II)-strong phosphoric acid and strong phosphoric acid in the same way as has been reported previously.[7]

Results and Discussion

Establishment of Equilibration. *(1) Equilibrium Composition of the Gas Phases*: The equilibrium composition of the gas phase at 1100, 1250, and 1300 °C was obtained by means of a digital computer using the linear programing method of White *et al.*[8] and using the thermodynamic data on the chemaical species (H_2, CO_2, CO, H_2O, O_2, SO_3, SO_2, SO, S_2, HS, H_2S,

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[1] C. J. B. Fincham and F. D. Richardson, *Proc. Roy. Soc. Ser. A*, **223**, 40 (1954).

[2] G. R. St. Pierre and J. Chipman, *Trans. AIME*, **206**, 1474 (1956).

[3] E. T. Turkdogan and L. S. Darken, *ibid.*, **221**, 464 (1961).

[4] S. Holmquist, *J. Amer. Ceram. Soc.*, **47**, 467 (1966).

[5] B. Iwasaki and T. Katsura, This Bulletin, **40**, 554 (1967).

[6] T. Kiba, T. Takagi, Y. Yoshida, and I. Kishi, *ibid.*, **28**, 641 (1955).

[7] S. Nagashima, M. Yoshida, and T. Ozawa, *ibid.*, **45**, 3446 (1972).

[8] W. B. White, S. M. Johnson, and G. B. Dantzig, *J. Chem. Phys.*, **28**, 751 (1958).

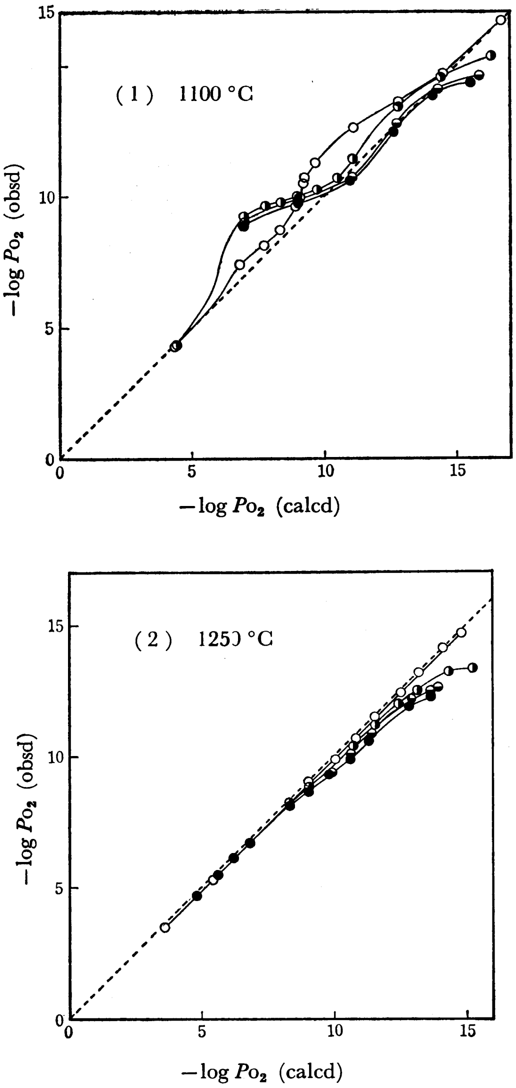

Fig. 1. Relationship between measured oxygen partial pressure and calculated oxygen partial pressure.

○ $(SO_2)_l$ 0 (0 cc/sec)
◑ 0.5% (0.03 cc/sec)
◒ 1.3% (0.08 cc/sec)
● 2.1% (0.13 cc/sec)

COS, CS, CS_2); the values of the standard free energy of the formation of each gas species were taken from "JANAF" Thermochemical Tables.[9] A HITAC-8500 was used for the computations.

Since it is not feasible to confirm whether the actually-established partial pressure of each gaseous species coincides with the thermodynamically-calculated value, the actual oxygen partial pressure was measured for each gas mixture by using a solid electrolyte composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$,[10,11] and the establishment of equilibration was judged through a comparison of the measured value with the calculated one.

A comparison of the measured oxygen partial pressure, P_{O_2}(obsd), with the calculated one, P_{O_2}(calcd) is given in Fig. 1(1) and -(2). As Fig. 1(1) shows, at 1100 °C the measured oxygen partial pressures deviate greatly from the values calculated by the thermodynamic data; this suggests a significant deviation from the equilibrium state within the gas phase. On the other hand, as is shown in Fig. 1(2), at 1250 °C the measured values are in fairly good agreement with the calculated ones, although they deviate slightly with a decrease in the oxygen partial pressure and with an increase in the $(SO_2)_l$ concentration. The results at 1300 °C were almost the same as those at 1250 °C. Therefore, at 1250 and 1300 °C the gas phase is considered to be approximately in equilibrium. The present study was mainly carried out at relatively high oxygen partial pressures above 10^{-12} atm P_{O_2} at 1250 and 1300 °C. The calculated P_{O_2} was adopted except for that at 1100 °C.

(2) Equilibration between Melts and the Gas Phase: The equilibrium amount of total sulfur in the melt was determined by varying the reaction time and by using various starting samples with the same Na_2O/SiO_2 ratio but containing different amounts of sulfur. Examples of the results are given in Fig. 2. The Na content of each sample after heating was analyzed to prove it to be unchanged in the bulk composition throughout the reaction.

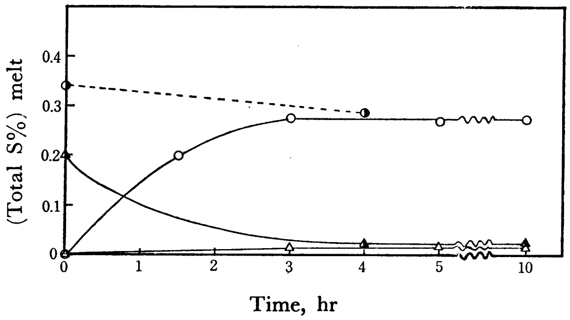

Fig. 2. Saturation time and sulfur content of Na_2O-SiO_2(1: 2) melts at 1250 °C.

○◑} $(CO_2)_l$: 6 cc/s
△▲} $(CO_2)_l$: 6 cc/s
$(H_2)_l$: 0.1 cc/s
in all cases, $(SO_2)_l$ is fixed to 0.03 cc/s.

Experiments at 1100 °C. Preliminary experiments were performed at 1100 °C, although, as was mentioned above, the gas phase was not equilibrated at this temperature. The solubility of gaseous species in silicate and phosphate melts has been studied by several investigators.[4,12-13] Of these, Pearce[12] studied the solubility of CO_2 in Na_2O-SiO_2 melts and observed that the solubility of CO_2 increases with an increase in the Na_2O/SiO_2 ratio. He explained that the solubility of CO_2 depends on the oxygen-ion activity ($a_{O^{2-}}$) in the melts.

In the present study, the solubility of sulfur decreases rapidly with a decrease in the oxygen partial pressures, ranging from 10^{-5} to 10^{-10} atm P_{O_2}, when the Na_2O/SiO_2 ratio is constant, while the solubility

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[9] "JANAF" Thermochemical Tables. U. S. Department of Commerce/National Bureau of Standards, (1965—1966).
[10] T. Katsura and M. Hasegawa, This Bulletin, **40**, 561 (1967).
[11] K. Shibata, *ibid.*, **40**, 830 (1967).
[12] M. L. Pearce, *J. Amer. Ceram. Soc.*, **47**, 342 (1964).
[13] A. Kato, R. Nishibashi, M. Nagano, and I. Mochida, *ibid.*, **55**, 183 (1972).

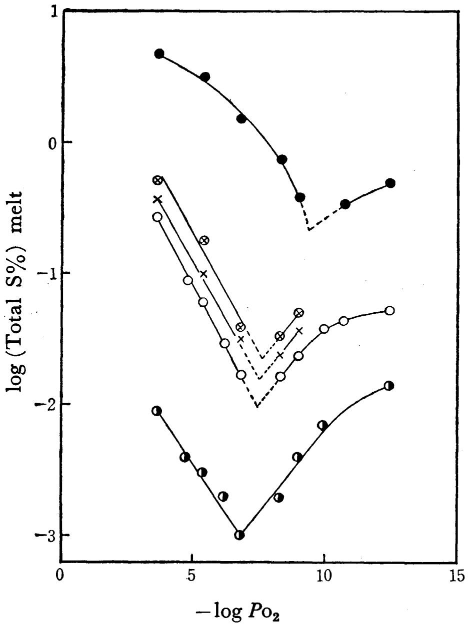

Fig. 3. Variation of sulfur content of Na_2O-SiO_2 melts with oxygen partial pressure at 1250 °C.
Na_2O-SiO_2 (1:1) melts
● $(SO_2)_i$: 0.5%
Na_2O-SiO_2 (1:2) melts
⊗ $(SO_2)_i$: 2.1%
× 1.3%
○ 0.5%
Na_2O-SiO_2 (1:3) melts
◑ $(SO_2)_i$: 0.5%
These symbols are also used in Figs. 3—8.

remains substantially constant though the P_{O_2} value decreases from 10^{-10} to 10^{-15} atm except for the case of $Na_2O/SiO_2=1$. These results are very different from those by Fincham and Richardson.[1] The difference can not be well explained, since the gas phase deviated far from the equilibrium state.

Experiments at 1250 °C. *(1) The Solubility of Sulfur Affected by the Oxygen Partial Pressure*: Fig. 3 shows the relationship between the solubility of sulfur in sodium silicate melts and the oxygen partial pressure at 1250 °C. The solubility increases greatly with an increase in the Na_2O/SiO_2 ratio, in the same way as was seen at 1100 °C, when the $(SO_2)_i$ concentration is constant. The solubility increases with an increase in the $(SO_2)_i$, as shown in Fig. 3, when the Na_2O/SiO_2 value is 1/2. When both the Na_2O/SiO_2 ratio in the melts and the $(SO_2)_i$ concentration are constant, the solubility shows its minimum at a specific oxygen partial pressure. Fincham and Richardson[1] also obtained the minimum solubility of sulfur in the CaO–Al_2O_3–SiO_2 systems and presumed the following two equilibria:

$$\frac{1}{2}S_2+\frac{3}{2}O_2+(O^{2-})_{\text{melt}}=(SO_4^{2-})_{\text{melt}} \qquad (1)$$

$$K_1=\frac{a_{SO_4^{2-}}}{P_{S_2}^{1/2}P_{O_2}^{3/2}a_{O^{2-}}}$$

$$\frac{1}{2}S_2+(O^{2-})_{\text{melt}}=(S^{2-})_{\text{melt}}+\frac{1}{2}O_2 \qquad (2)$$

$$K_2=\frac{P_{O_2}^{1/2}a_{S^{2-}}}{P_{S_2}^{1/2}a_{O^{2-}}}$$

If the oxygen ion activity of the melts, $(a_{O^{2-}})$, is constant in the constant melt composition and at a given temperature, and if, in addition, the activities of SO_4^{2-} and S^{2-} in the melt are proportional to the total sulfur concentrations, $(\%\ S)_{\text{melt}}$, the equilibrium constants, K_1 and K_2, may be written as K_1' and K_2' respectively:

$$K_1'=\frac{(\%S)_{\text{melt}}}{P_{S_2}^{1/2}P_{O_2}^{3/2}} \qquad (1)'$$

$$K_2'=\frac{P_{O_2}^{1/2}(\%S)_{\text{melt}}}{P_{S_2}^{1/2}} \qquad (2)'$$

Figure 4 illustrates the relationship between the apparent equilibrium constants, K_1' and K_2', and the oxygen partial pressure on the basis of the present experiments. The results show that $\log K_1'$ is almost constant at high oxygen partial pressures, and that $\log K_2'$ is almost constant at low oxygen partial pressures, although the constant, K_1', varies somewhat in the case of melts with the Na_2O/SiO_2 ratio of 1/1 at high oxygen partial pressures. This suggests that the sulfur dissolves as sulfate at high oxygen partial pressures and as sulfide at low oxygen partial pressures.

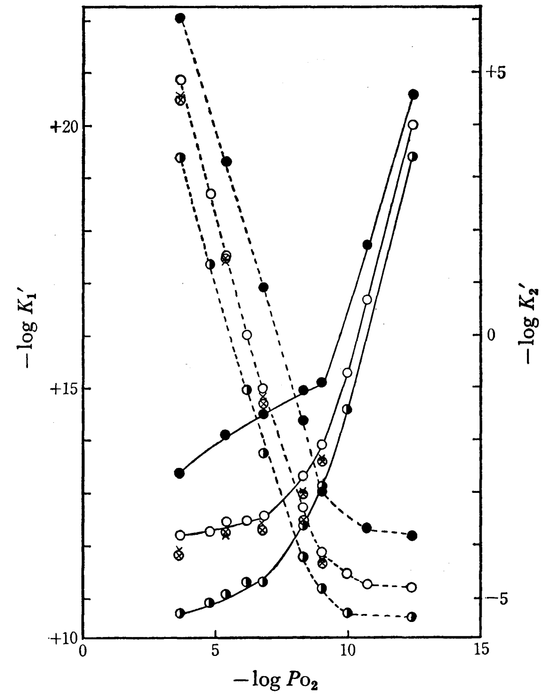

Fig. 4. Sulfate (K_1')(——) and sulfide (K_2')(----) equilibrium constants as a function of oxygen partial pressure for Na_2O-SiO_2 melts at 1250 °C.

(2) Relationship between the Solubility of Total Sulfur and the Partial Pressures of the Sulfur Compounds: The relationship between the solubility of sulfur in the melts and the calculated partial pressures of various sulfur compounds in the gas phase was examined. Figs. 5-(1) and -(2) show the relationship between the total sulfur content of the melts, and P_{SO_3} and P_{H_2S}, respectively. The number in parentheses placed close to each individual point indicates the value of $-\log P_{O_2}$. However, in order to avoid illegibility, the values are omitted at some points in the figures.

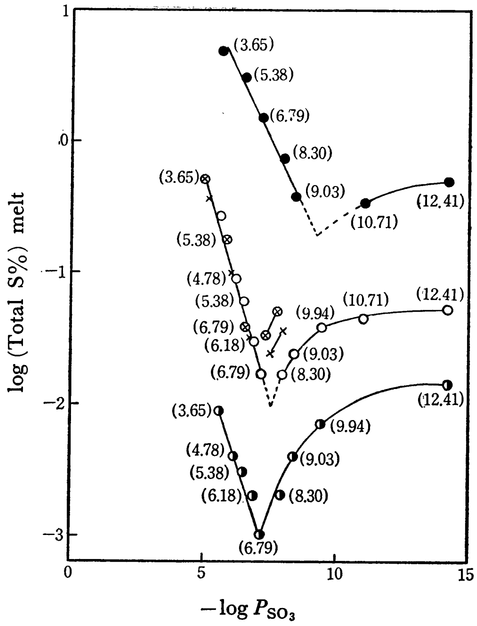

Fig. 5(1). Variation of sulfur content of Na_2O-SiO_2 melts with P_{SO_3} at 1250 °C.

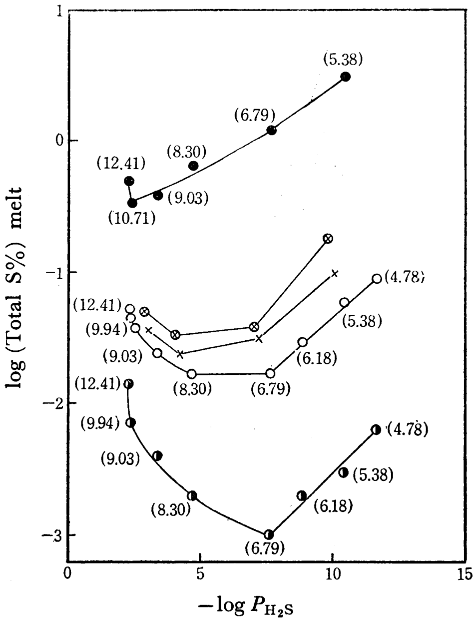

Fig. 5(2). Variation of sulfur content of Na_2O-SiO_2 melts with P_{H_2S} at 1250 °C.

As may be seen in Fig. 5-(1), the total sulfur content of a melt increases with an increase in P_{SO_3} at relatively high oxygen partial pressures; this relation may be expressed as a linear equation as follows:

$$\log (\%\ S)_{\text{melt}} = k_1 + (0.7\sim0.75) \times \log P_{SO_3} \qquad (3),$$

where k_1 is constant and where Equation (3) is applicable in the range above 10^{-9} atm P_{O_2} when the Na_2O/SiO_2 ratio is 1/1 and in the range above $10^{-6.8}$ atm P_{O_2} when the Na_2O/SiO_2 ratios are 1/2 and 1/3. These results support the idea that the sulfur dissolves mainly as sulfate at high oxygen partial pressures. On the other hand, as is shown in Fig. 5-(2), the total sulfur content of a melt increases with an increase in P_{H_2S} at relatively low oxygen partial pressures, though we can not obtain a simple equation such as has just been obtained at relatively high oxygen partial pressures. However, this trend may also support the idea that the total sulfur may dissolve mainly as sulfide at low oxygen partial pressures.

The relationships between the solubility of sulfur and the sulfur compounds in the gas phase other than SO_3 and H_2S were also examined, but the relationships showed significant discrepancies in all cases from the general rules expected thermodynamically.

(3) Determination of Sulfide- and Sulfate-Sulfur in Melts: One of the most direct and definite methods to distinguish the state of dissolved sulfur in a melt is to chemically analyze the sulfide- and sulfate-sulfur separately. The method of determining sulfide and sulfate has been established, as has been mentioned before.[7] Here, in Table 1 we show some analytical results in the case of the Na_2O/SiO_2=1/2.

As may clearly be seen in Table 1, the total sulfur is mostly in the form of sulfate at higher oxygen partial pressures (above $10^{-6.8}$ atm P_{O_2}). On the other hand, at lower oxygen partial pressures (below 10^{-9} atm P_{O_2}), the total sulfur is mostly in the form of sulfide.

TABLE 1. SULFIDE- AND SULFATE-SULFUR CONTENT OF Na_2O-SiO_2 (1:2) MELTS AT 1250°C

$(SO_2)_i$: 0.5% (0.03 cc/sec)					
$(CO_2)_i$ (cc/s)	$(H_2)_i$	−log P_{O_2} (calcd.)	Total-S	Sulfide-S	Sulfate-S
6	0	3.65	0.27	<0.001	0.27
	0.02	5.38	0.060	<0.001	0.060
	0.1	6.79	0.017	0.001	0.016
5.5	0.5	8.30	0.017	0.008	0.009
5	1	9.03	0.024	0.021	0.003
3	3	10.71	0.044	0.042	0.002
1	5	12.41	0.053	0.052	0.001

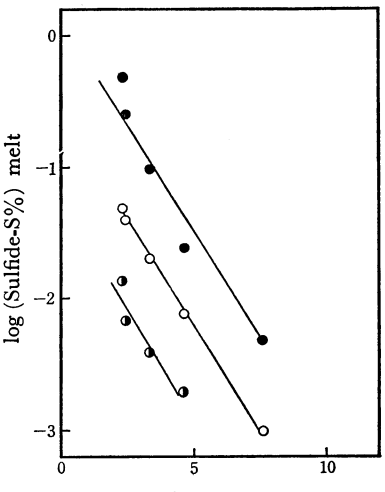

Fig. 6. Variation of sulfide-sulfur content of Na_2O-SiO_2 melts with P_{H_2S} at 1250 °C.

Fig. 6 shows the relationship between the analyzed sulfide-sulfur content in the melts and P_{H_2S}. As may be seen in Fig. 6, the sulfide-sulfur content increases almost linearly with an increase in P_{H_2S}, leading to the following equation:

$$\log(\%\ S)_{\text{melt}} = k_2 + 0.3 \times \log P_{H_2S},$$

where k_2 is constant.

This fact proves the thermodynamic prediction that sulfur should dissolve in the form of sulfide when the melt was at relatively low oxygen partial pressures.

Effect of the Temperature on the Solubility of Sulfur. Figure 7 shows the relationship between the sulfur content of the sodium silicate melts and the oxygen partial pressure at 0.5% of $(SO_2)_i$ and at 1250 and 1300 °C. As may be seen in Fig. 7, the minimum point of the solubility moves in the direction of higher oxygen partial pressures as the temperature increases. Fig. 7 indicates that the increase in the solubility of the total sulfur does not necessarily correspond to the temperature change. This is because the partial pressure of each sulfur compound varies according to the temperature change. The experimental results at 1100 °C were complicated, since the gas phase was not in the chemical equilibrium state. However, in some experiments at 1100 °C, *i.e.*, under the conditions of $(CO_2)_i$: 6 cc/s and $(SO_2)_i$: 0.03 cc/s, the measured oxygen partial pressure showed a good agreement with the calculated value [$P_{O_2}(\text{obsd}) = 10^{-4.33}$ atm, $P_{O_2}(\text{calcd}) = 10^{-4.35}$ atm], and the results corresponded reasonably to the experiments at 1250 and 1300 °C, *i.e.*, under the conditions of $(CO_2)_i$: 6 cc/s and (SO_2): 0.03 cc/s. At these three temperatures, P_{SO_2} and P_{SO_3} were nearly the same and were calculated to be $10^{-2.3}$ atm and $10^{-5.6}$ atm respectively. In Fig. 8, the sulfate content in each melt is plotted against $1/T$, where T is the absolute temperature. This shows that the solubility of the sulfate decreases with an increase in the temperature. Moreover, from Fig. 8, the following empirical equations were obtained:

$$\log(\%S)_{\text{melt}} = 0.76 \times \frac{10^4}{T} - 4.2$$

for Na_2O-SiO_2 (1:1) melt

$$\log(\%S)_{\text{melt}} = 1.16 \times \frac{10^4}{T} - 8.1$$

for Na_2O-SiO_2 (1:2) melt

$$\log(\%S)_{\text{melt}} = 1.74 \times \frac{10^4}{T} - 13.4$$

for Na_2O-SiO_2 (1:3) melt

The change in solubility with the temperature can be written as in following equation[14]: $R \ln a = \bar{L}/T +$ constant, where R is the gas constant, a is the activity of solute, and $\bar{L}$ is the relative partial molal enthalpy of a solution. When this equation is compared with the above three ones, it is found that the relative partial molal enthalpies have positive values. However, the change in the solubility of sulfur in the form of sulfide with the temperature is complicated, and it was impossible to obtain a simple relation similar to that obtained above for the sulfate solubility.

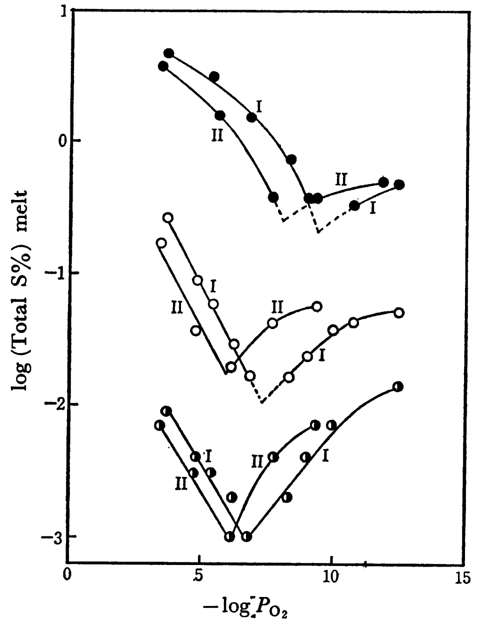

Fig. 7. Variation of sulfur content of Na_2O-SiO_2 melts with partial pressure of oxygen at 1250 °C and 1300 °C and at 0.5% of $(SO_2)_i$. I at 1250 °C, II at 1300 °C.

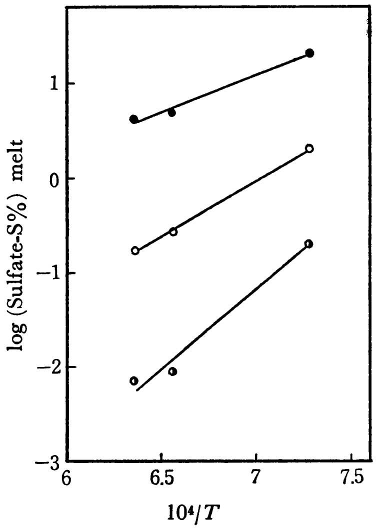

Fig. 8. Change of sulfate-solubility with temperature. [$(CO_2)_i$: 6 cc/sec, $(SO_2)_i$: 0.03 cc/s]

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[14] G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York (1961), p. 393.