Original Paper

Sulfur chemistry in a borosilicate melt

Part 2. Kinetic properties[1]

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The diffusion of gaseous sulfur compounds under both oxidizing and reducing conditions has been determined in an alkali borosilicate melt representative of compositions under consideration for nuclear waste immobilization. The diffusion coefficients D of these sulfur gases as a function of melt temperature T (in K) can be expressed as:

$$\log D = -3.08 - (3300/T)$$

regardless of whether the sulfur is being incorporated as the sulfate ion in oxidized melts or as the sulfide ion in reduced melts. The rate-determining step for the diffusion is probably the diffusion of SO_2 gas into the melt. Even though sulfate and sulfide ions are the two equilibrium redox states of sulfur in this melt, transient sulfur species of intermediate redox state can be produced in the melts by placing an initially oxidized melt in a reduced sulfur atmosphere. Metastable polysulfide ions of the general formula S_x^{2-} and S_y^- are formed which slowly decay to the more stable sulfide ions under these conditions.

Chemismus des Schwefels in einer Borosilicatschmelze

Teil 2. Kinetische Eigenschaften

Die Diffusion von gasförmigen Schwefelverbindungen sowohl unter oxidierenden als auch unter reduzierenden Bedingungen wurde in einer Alkali-Borosilicatschmelze mit einer Zusammensetzung bestimmt, wie sie für die Lagerung radioaktiven Abfalls in Betracht kommt. Die Diffusionskoeffizienten D dieser Schwefelgase als Funktion der Schmelztemperatur T (in K) können ausgedrückt werden durch:
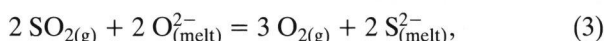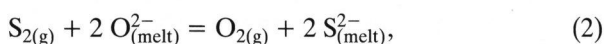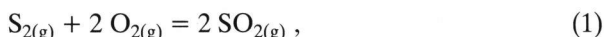
$$\log D = -3{,}08 - (3300/T),$$

unabhängig davon, ob der Schwefel als Sulfation in oxidierten Schmelzen oder als Sulfidion in reduzierten Schmelzen eingebaut ist. Der geschwindigkeitsbestimmende Schritt für die Diffusion ist wahrscheinlich die Diffusion von SO_2-Gas in die Schmelze. Obwohl Sulfat- und Sulfidionen die beiden Redoxgleichgewichtszustände von Schwefel in dieser Schmelze sind, können Übergangsformen des Schwefels in Redoxzwischenstadien entstehen, wenn eine ursprünglich oxidierte Schmelze in eine reduzierte Atmosphäre eingebracht wird. Es bilden sich metastabile Polysulfidionen der allgemeinen Form S_x^{2-} und S_y^-, die unter diesen Bedingungen langsam in die stabileren Sulfidionen zerfallen.

1. Introduction

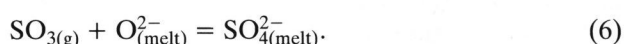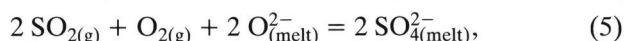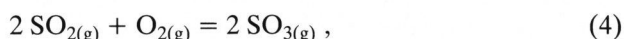### 1.1. Equilibrium properties of sulfur in glass melts

Under reducing conditions, sulfur dissolves in a borosilicate melt as the sulfide ion. This is governed by the following set of solvolysis reactions:

$$S_{2(g)} + 2\,O_{2(g)} = 2\,SO_{2(g)}, \tag{1}$$

$$S_{2(g)} + 2\,O^{2-}_{(melt)} = O_{2(g)} + 2\,S^{2-}_{(melt)}, \tag{2}$$

$$2\,SO_{2(g)} + 2\,O^{2-}_{(melt)} = 3\,O_{2(g)} + 2\,S^{2-}_{(melt)}, \tag{3}$$

which describe the interaction of the sulfur-containing gases with the oxide ions of the melt [1 and 2]. The solubility of sulfur as the sulfide ion in the melt is constrained to increase as the melt temperature increases and as the imposed oxygen fugacity decreases; that is, sulfide solubility increases with conditions that become more reducing.

When a borosilicate melt is melted under oxidizing conditions, the sulfur is incorporated into the melt structure as the sulfate ion. This solution of sulfur in an oxidized melt can be described by the reactions [1 and 2]:

$$2\,SO_{2(g)} + O_{2(g)} = 2\,SO_{3(g)}, \tag{4}$$

$$2\,SO_{2(g)} + O_{2(g)} + 2\,O^{2-}_{(melt)} = 2\,SO^{2-}_{4(melt)}, \tag{5}$$

$$SO_{3(g)} + O^{2-}_{(melt)} = SO^{2-}_{4(melt)}. \tag{6}$$

Unlike the solubility of sulfur as the sulfide ion, the solubility of sulfur as the sulfate ion in a borosilicate melt will increase with a decrease in melt temperature and with an increase in imposed oxygen fugacity. Conditions that are more oxidizing will result in an enhanced solubility of the sulfate ion in the melt.

As a consequence of the solubility relations that govern the dissolution of sulfur as sulfide ions and as sulfate ions in melts, there exists a point of minimum solubility of sulfur at an intermediate oxygen fugacity for melts at constant temperature. This region of minimum solubility also corresponds to the position at which sulfate ions are in equilibrium with the sulfide ions in the melt [1 and 2]. At a particular temperature, the range of oxygen fugacities over which sulfate and sulfide ions coexist is quite small.

1.2. Glass processing

Such information on the solubility and redox state of sulfur in silicate melts is important in understanding the fining of flint (oxidized) and amber (reduced) sulfur-containing glasses [2 and 3]. In addition, since sulfur is one of many elements to be incorporated in glass during the immobilization of nuclear waste, these equilibrium properties of sulfur set key constraints on the processing of the melt with respect to foaming and sulfide precipitation [1 and 4 to 6]. However, in the processing of glass melts, not only are equilibrium considerations of importance but also kinetic properties such as diffusion. The fining of commercial glasses and the incorporation of sulfur in nuclear waste glasses may depend on a) the solubility of sulfur as a function of melt temperature, imposed oxygen fugacity, glass composition, and sulfur content of the atmosphere [1], b) the diffusion of the gaseous sulfur compounds into or out of the melt as a function of the same variables [7], and c) the formation of transient sulfur species (other than sulfate and sulfide ions) in the glass melt under certain redox conditions.

2. Objectives

Savannah River Laboratory glass frit no. 131 (SRL-131) was used as the reference composition for this study, since not only has its redox chemistry been extensively characterized [8] but also its properties with respect to solubility and diffusion of gases [1 and 9]. SRL-131 is an alkali borosilicate composition that is (wt%): 57.9 SiO_2, 1.0 TiO_2, 0.5 ZrO_2, 14.7 B_2O_3, 0.5 La_2O_3, 2.0 MgO, 5.7 Li_2O, and 17.7 Na_2O and is representative of those glass compositions under consideration for the immobilization of nuclear waste [6 and 10].

The specific objective of this study is two-fold: first, to ascertain the diffusion of sulfur in oxidized (sulfate-containing) versus reduced (sulfide-containing) SRL-131 melts as a function of the melt temperature and to compare this diffusion to that of other gases such as oxygen and water vapor in this melt, and second, to ascertain the kinetic stabilization of transient sulfur species such as sulfite ions [11], elemental sulfur [12], and polysulfide ions [13] in SRL-131 melts since all have been previously iden-

tified in other glasses. It should be emphasized that the base composition, SRL-131, is iron-free; and as such, mutual interactions of sulfur with the important redox species of iron were not considered in this study. This will be the subject of part 3 of this series on sulfur chemistry in borosilicate melts.

3. Experimental procedures

3.1. Diffusion of gaseous sulfur compounds into melts

The measurement of the diffusion coefficient for sulfur gases into the glass-forming SRL-131 melt was accomplished similar to prior studies for the diffusion of oxygen [14 and 15] and water vapor [16] into SRL-131 melts. Spherical beads of SRL-131 glass were prepared on rings of platinum metal [1]; the rings were of constant diameter (4.5 mm) and contained a constant amount of SRL-131 glass (0.25 g). These molten glass spheres of constant geometry were kept on the ring by surface tension. The melts were initially equilibrated for 4 to 14 h in a pure CO_2 atmosphere, which provided relatively oxidizing conditions, or in a 15 % CO_2/85 %CO atmosphere, representative of relatively reducing conditions, at one of the two melt temperatures (1150 or 1050 °C). Previous studies [1] had shown that the imposed oxygen fugacity of the CO_2 atmosphere would incorporate sulfur as the sulfate ion in the melt whereas the CO_2/CO mixture resulted in sulfur being present as the sulfide ion. Several series of glasses were thus produced, each consisting of samples of constant geometry prepared at the same oxygen fugacity and melt temperature, but not yet exposed to a sulfur-containing atmosphere.

Individual samples were then reinserted into the furnace at the same melt temperature as their initial synthesis but in an atmosphere now containing 15 % SO_2 in addition to the CO_2 or the CO_2/CO mixture. Thus, for these samples initially equilibrated for oxygen content, sulfur was allowed to diffuse from the atmosphere into the spherical melts. These melts were quenched as a function of time exposed to the sulfur-containing atmosphere, so as to freeze in the amount of sulfur that had diffused in the melts. Diffusion was the mode of transport of the sulfur gas into the melt since these melts were essentially static systems in which convection was held to a minimum [14 and 15].

The total sulfur content was determined in the samples synthesized under oxidizing conditions. This procedure involved the digestion of the glass powder, reduction of all sulfur in the glass (present as sulfate) to sulfide in the digestion solution, distillation of the sulfide as H_2S gas, trapping the H_2S in a buffer solution, and determination of the sulfide content by a calibrated specific ion electrode [1]. The total sulfur content as well as sulfide ion content was determined

in the samples synthesized under reducing conditions. The total sulfur content was measured by the specific ion electrode technique. The sulfide ion content was determined by an iodometric titration (to measure the total reducing power of the glass; in essence, the sulfide ion concentration) or by a spectrophotometric measurement of the yellow coloration in the glass (as sulfide induces this color) [1].

Each series of samples synthesized at a particular temperature and oxygen fugacity provided the determination of sulfur (or sulfide) content of the glasses as a function of the time allowed for the sulfur to diffuse in the melts. This diffusion process could also be modeled by the solution of Fick's Law of Diffusion for a diffusing gas through a spherical surface into a liquid [1 and 17]. Accordingly, then, the diffusion of the gas (sulfur) into the glass melt could be followed as a function of the time for different assumed diffusion coefficients of the gas. The experimental results were thus compared to the diffusion model calculations to provide an estimate of the diffusion coefficient [14 to 16].

To illustrate that diffusion was indeed the operational process for the incorporation of sulfur into the glass melts, a sample of SRL-131 glass was placed within a cylindrical platinum capsule open on one end. As before, the melt was equilibrated with respect to oxygen fugacity at 1150 °C under reducing conditions (15 % CO_2/85 % CO). The sulfur-containing atmosphere was then allowed to diffuse for 3 h through the flat melt surface into a cylindrical melt charge. The diffusion front could then be visually observed by the yellow coloration of the sulfide ion resulting from the incorporation of the diffusing sulfur into the melt. This color boundary of yellow, S^{2-}-containing, to colorless SRL-131 glass with the absence of visible convection currents should prove that diffusion is indeed the mode of sulfur transport through the glass melt [15 and 18].

3.2. Kinetic control of transient sulfur species in melts

Samples were synthesized similar to those in the diffusion study except that instead of being pre-equilibrated with respect to oxygen fugacity, they were initially melted in air, a more oxidizing environment than that for their final syntheses. These samples were then placed in the atmosphere containing 5 or 15 % SO_2 with the reducing 15 % CO_2/85% CO gas mixture and subsequently quenched as a function of melt time. Thus, the samples were initially supersaturated in oxygen content. As a function of time, the oxygen should diffuse out of the melts and the sulfur should diffuse into the melts where it is eventually incorporated as the sulfide ion.

These samples were analyzed for total sulfur content by the specific ion electrode procedure, for
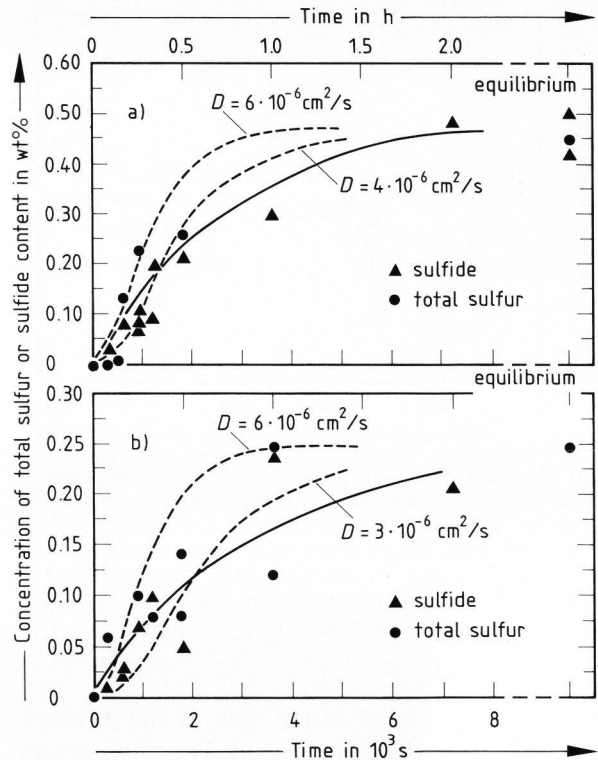
Figures 1a and b. Diffusion of sulfur into SRL-131 melts of constant spherical geometry ($r = 0.225$ cm) under reducing conditions at a) 1150 °C and $-\log f_{O_2} = 12$, b) 1050 °C and $-\log f_{O_2} = 14$. Diffusion curves for the sulfur gas responsible for diffusion as for Fick's Law of Diffusion of appropriate diffusion coefficients D are provided according to the model.

the sulfide ion or reduced sulfur content by the iodometric titration, and for the presumed sulfide ion by the spectrophotometric procedure [1].

4. Results

4.1. Diffusion of sulfur under reducing conditions

Figures 1a and b show the experimental data for the diffusion of the sulfur gases into SRL-131 melt under reducing conditions such that the sulfur is being incorporated as the sulfide ion. Qualitatively, it was quite evident that the samples were becoming darker yellow (more sulfide) with time. These data are compared to the theoretical model for diffusion of a gas through a spherical surface of a liquid, with the sulfur content predicted as a function of the time for several gaseous diffusion coefficients. At 1150 °C, the model diffusion coefficient is determined to be $4 (\pm 2) \cdot 10^{-6}$ cm²/s; while at 1050 °C, the diffusion coefficient for the sulfur gas is $3 (\pm 2) \cdot 10^{-6}$ cm²/s. Unfortunately, the precision of the data results in appreciable experimental error for the measured diffusion coefficients.

The diffusion of the gaseous sulfur compound under these reducing conditions is also demonstrated by the color boundary results of figure 2. The diffusion is herewith traced by the color of the sulfide

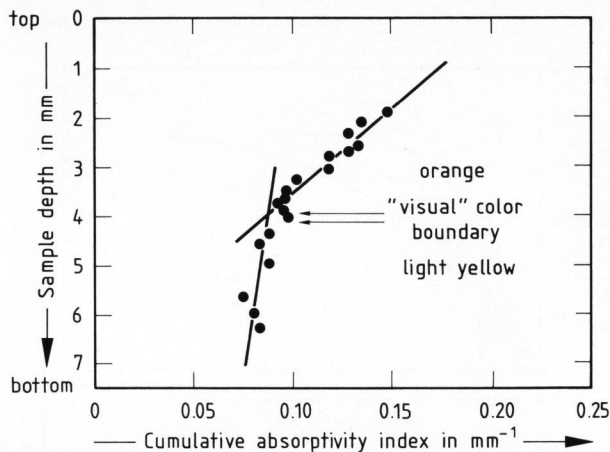Henry D. Schreiber; Samuel J. Kozak; Paul G. Leonhard; Kimberly K. McManus; Charlotte W. Schreiber:
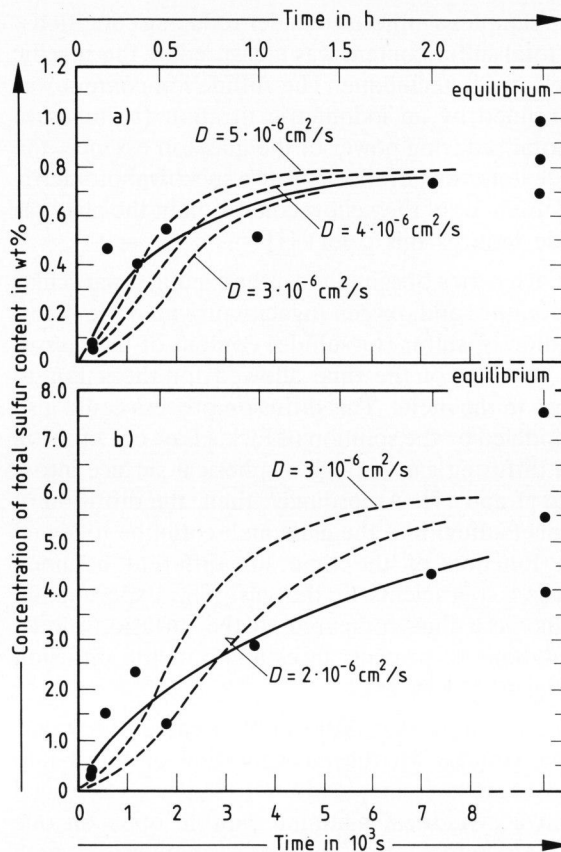
Figure 2. Color boundary method to ascertain the diffusion coefficient of sulfur gas under reducing conditions (cumulative absorption index, top through depth at $\lambda = 500$ nm). Sulfide provides yellow-orange coloration as it is incorporated into the glass melt structure. (SRL-131, 1150 °C, 5 % SO_2 at $-\log f_{O_2} = 12.6$, 0.4 g in cylindrical container of 0.75 cm depth, diffusion through flat surface for 3 h.)

ion which is produced in the melt as the diffusion front advances to depth in the melt. The colored layer is quite evident on top of the colorless sulfur-free bottom; proof that diffusion is the rate-determining step in these systems. The position of the color boundary or diffusion front can be determined visually or spectrophotometrically as shown in figure 2. The depth of the diffusion front for the time exposed to the sulfur-containing atmosphere is consistent with the diffusion coefficient determined from the results of figure 1a and as applied to Fick's Law of Diffusion through a flat surface into a melt.


Figures 3a and b. Diffusion of sulfur into SRL-131 melts of constant spherical geometry ($r = 0.225$ cm) under oxidizing conditions at a) 1150 °C and $-\log f_{O_2} = 4.1$, b) 1050 °C and $-\log f_{O_2} = 4.5$. Diffusion curves for the sulfur gases as for Fick's Law of Diffusion of appropriate diffusion coefficients D are provided according to the model. At 1050 °C, a sulfate-rich layer formed on the surface of the sphere and grew into the sphere with time.

4.2. Diffusion of sulfur under oxidizing conditions

Figures 3a and b illustrate the experimental data for the diffusion of sulfur as it is incorporated as the sulfate ion in SRL-131 melts as a function of the time and temperature. By comparison of these experimental results with the predictions of the diffusion model, the diffusion coefficient of the gaseous sulfur species is ascertained to be about $4 (\pm 2) \cdot 10^{-6}$ cm²/s at 1150 °C and about 2.5 $(\pm 2) \cdot 10^{-6}$ cm²/s at 1050 °C. However, at the lower melt temperature, a devitrified sulfate layer was observed on all quenched samples − indicative that a molten sulfate layer [19] was forming on the spherical samples and that the layer was growing as a function of time exposed to the sulfur atmosphere. Thus, at this lower temperature, the measured diffusion coefficient may not be representative of diffusion through the SRL-131 melt per se but rather through the forming sulfate layer.

All sulfur for the samples in figures 1a and b was incorporated in the glass as the sulfide ion, whereas that for samples in figures 3a and b was as the sulfate ion. The imposed oxygen fugacities were sufficiently

separated from the position of the sulfide-sulfate coexistence in the melt so that each series contained sulfur as just one of the two ions. It was assumed that there was no dependence of the gaseous sulfur species diffusion coefficient with imposed oxygen fugacity for the oxidized set (as long as sulfate was present) or for the reduced set (as long as sulfide was present).

4.3. Kinetic control of transient sulfur species in melts

The results for the kinetic studies whereby the samples initially supersaturated in oxygen are remelted as a function of time under reducing conditions containing a sulfur atmosphere are shown in figures 4a and b for 1150 °C and in figures 4c and d for 1050 °C. Almost immediately these samples became colored very dark amber, almost as if a very dark iron-sulfur amber color [20] was being formed (but no iron was present in these glasses, and the analyzed iron content was less than 0.002 wt% − the limit of detection). The dark amber color then decreased in intensity with time until the yellow coloration of the
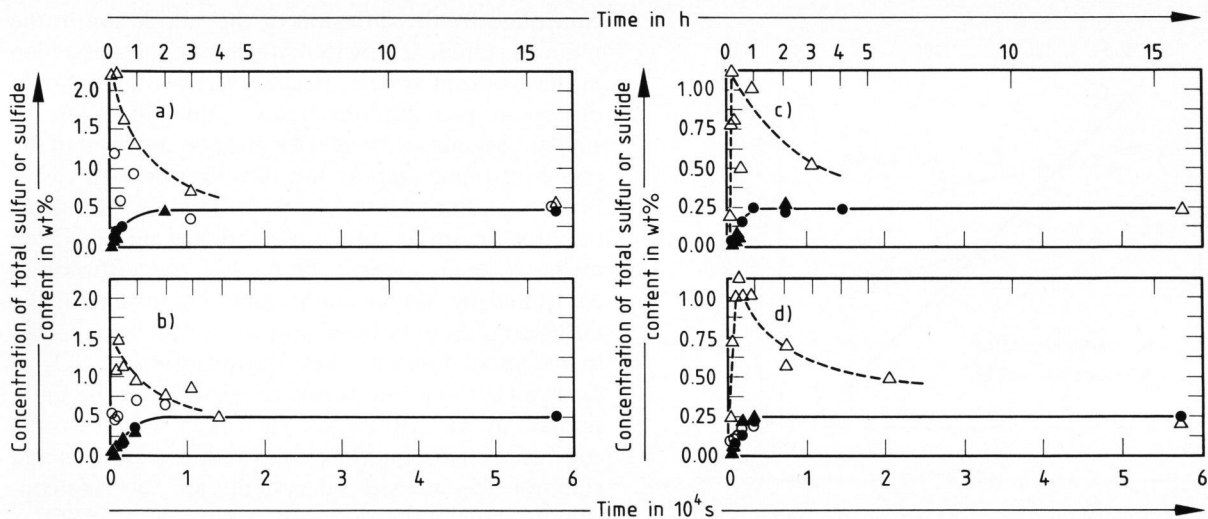
Figures 4a to d. Incorporation of sulfur into SRL-131 melts of spherical geometry under reducing conditions in $CO_2/CO/SO_2$ atmosphere at a) 1150 °C, 5 % SO_2, $-\log f_{O_2} = 12.6$; b) 1150 °C, 15 % SO_2, $-\log f_{O_2} = 12.6$; c) 1050 °C, 5 % SO_2, $-\log f_{O_2} = 14.1$; d) 1050 °C, 15 % SO_2, $-\log f_{O_2} = 13.5$. Pre-reduced samples as in figures 1a and b are represented by solid symbols and solid lines, while samples which were not equilibrated at the CO_2/CO atmosphere (possess the oxygen fugacity of air initially) and are consequently supersaturated in oxygen initially are given by the open symbols and dashed lines. Samples were analyzed for total sulfur, as well as for sulfide spectrophotometrically; circles represent total sulfur analyses, while triangles represent spectrophotometric sulfide analyses.

sulfide ion was present in the equilibrated samples at long times. Figures 4a and b show the sulfide content as inferred from the spectrophotometric calibration of the color and the total sulfur analyses of these samples. This spectrophotometric procedure obviously over analyzes the sulfide content of the glasses. The sulfur content of the melts is indeed almost instantaneously equilibrated (as compared to the sulfur diffusion previously determined and also shown for reference in figures 4a and b); probably due to the convection created by the simultaneous diffusion of oxygen out of the samples as sulfur gases diffuse into the samples. This process creates a transient colored sulfur species, which is probably more oxidized than the sulfide ion and which decays with time to the more stable sulfide ion at equilibrium. Figures 4c and d confirm the results of figures 4a and b in that the normal temperature dependencies are observed. At the lower temperature of figures 4c and d, it took a little longer for the transient colored sulfur species to form and also a little longer for it to decay to the equilibrium sulfide form.

Several of these dark amber glasses which resulted from the exposure of these oxygen supersaturated melts to a reduced sulfur atmosphere were analyzed for sulfide content by the spectrophotometric procedure as well as the iodometric procedure for reduced sulfur content. These results are shown in figure 5, which illustrate the transient sulfur species are too highly colored to be classified as sulfide ions. The color, spectroscopic properties, and the conditions of formation for these sulfur species are consistent with the existence of polysulfide (S_x^{2-} and S_y^{-}) ions in the SRL-131 melts [13 and 21]. The excess oxygen in the samples initially destabilizes the
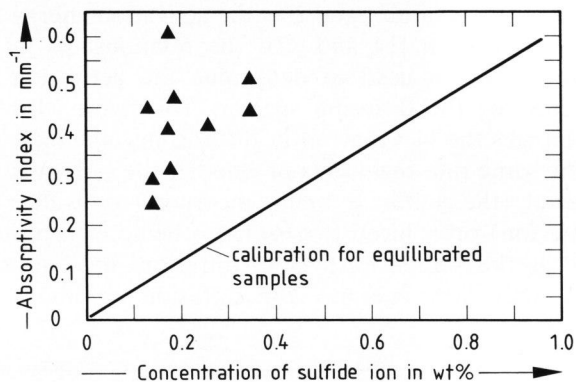

Figure 5. Unequilibrated amber samples (from figures 4a to d) analyzed for sulfide via spectral methods (at 420 minus 700 nm base line) and for total reduced sulfur by iodometric titration. The samples (solid symbols) were initially supersaturated in oxygen, then exposed to reducing sulfur atmosphere for short times.

formation of sulfide ions, but the reducing conditions preclude the formation of sulfate ions in the melt. Accordingly, the transient polysulfide ion of intermediate redox state becomes a metastable species in the melt under this kinetic control.

5. Discussion

5.1. Temperature dependence of the diffusion coefficient

The temperature dependence of the sulfur diffusion coefficient in SRL-131 melts is provided in figure 6 along with those of oxygen and water vapor in the same system. Since this thermal dependence can be expressed by an Arrhenius relationship:
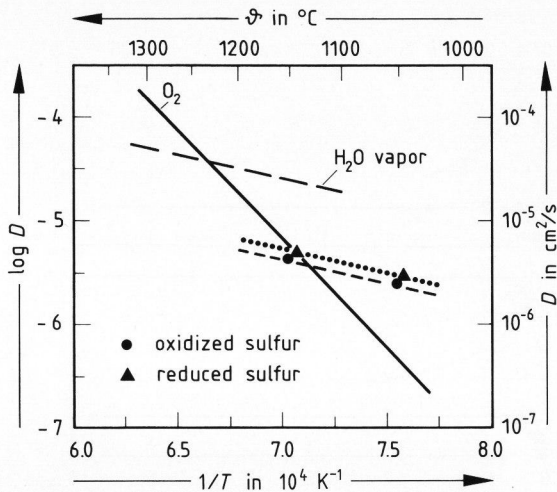
$$D = D_0 \, e^{-E/RT} \tag{7}$$

Figure 6. Temperature dependence of the sulfur diffusion coefficient (oxidized and reduced) as compared to the oxygen and water vapor diffusion coefficients in SRL-131 melts.

where D is the diffusion coefficient, D_0 is a constant typically related to the number of pathways available for diffusion, R is the ideal gas constant, T is the absolute temperature, and E is the activation energy for the diffusion [14 and 22]; the relationships in figure 6 can be used to determine the activation energies for the diffusing species. The figure also emphasizes the fact that sulfur diffuses into the melt via the same rate regardless of whether the system is oxidized (the sulfur is being incorporated as the sulfate ion) or reduced (the sulfur is being incorporated as the sulfide ion). Both diffusions have the same activation energies for diffusion of about 63 kJ/mol.

5.2. Comparison of gaseous diffusion coefficients

Oxygen and gaseous sulfur diffuse at about the same rate at 1150 °C, but gaseous sulfur is measurably faster than oxygen at 1050 °C according to figure 6. In addition, the activation energy for the diffusion of oxygen is over five times greater than that for gaseous sulfur through SRL-131 melt. The diffusion of water vapor through SRL-131 melt is about an order of magnitude faster than that for either oxidized or reduced sulfur vapor, but the activation energies for both processes are almost exactly the same.

These relationships among the diffusion coefficients of gaseous sulfur compounds, oxygen, and water vapor in SRL-131 melts are analogous to those previously compiled for soda-lime-silica melts [7].

5.3. Mechanism for diffusion of sulfur gases

That the gaseous sulfur species diffuse the same in oxidized and in reduced melts of SRL-131 implies that the diffusing species must be similar or the same in both cases. That is, the diffusion cannot be controlled by the diffusion of the sulfide ion in the reduced system and by the diffusion of the sulfate ion in the oxidized system, because the two ions should diffuse at two different rates. Thus, the same or similar gaseous sulfur species must be involved in the rate-controlling step of the diffusion in both cases. From equations (1 to 6) which describe the incorporation of sulfur into these reduced and oxidized melts, it then appears likely that the diffusion is controlled by SO_2 in both cases. For example, the diffusion of S_2 in reduced systems would be expected to be quite different than the diffusion of SO_3 in oxidized systems and would be expected to be more similar to O_2 diffusion. This then leads to the conclusion that equation (3) in reduced systems and equation (5) in oxidized systems are the rate-controlling steps in the diffusion process, so that SO_2 is the gaseous sulfur species for which this diffusion process is measuring. It is interesting that SO_2 as well as H_2O possess the same activation energy for diffusion, whereas O_2 has a significantly higher activation energy for diffusion. Both SO_2 and H_2O react with the melt by solvolysis reactions to be incorporated in the melts, while oxygen incorporation is more of a physical process. Thus, sulfur dioxide and water react with the melt and bump along in that fashion, while oxygen must force its way through available channels and holes in the melt − consistent with the lower activation energy for the former two gases. On the other hand, water diffuses faster because it is smaller than the sulfur gases and has more pathways for diffusion available to it.

5.4. Diffusion coefficients and glass processing

The result that SO_2 and O_2 diffuse at about the same rate at 1150 °C means that sulfur poses no real processing constraint with respect to diffusion at this temperature. The equilibration of oxygen as well as sulfur would be similar in glass melts for nuclear waste immobilization at this temperature. However, for commercial glass manufacture, the processing often occurs at a lower temperature where sulfur gases diffuse faster than oxygen. Thus, the ability of sulfur to sweep bubbles from glass melts may be in part due to its ability to diffuse from and into the melt faster at these temperatures. On the other hand, oxygen (based on its diffusing characteristics) may be a better refining agent at the higher temperatures in SRL-131 melts. For the total view of the fining process, nevertheless, these kinetic results must be understood within the context of gaseous solubility as a function of temperature and redox state [1].

5.5. Kinetic stabilization of the polysulfide ion

Even though part 1 of this series [1] on the chemistry of sulfur in SRL-131 melts demonstrated that the sulfate (oxidized) and sulfide (reduced) ions were the

stable entities incorporated in this borosilicate melt under equilibrium conditions, other transient sulfur species which may be stable for times up to several hours can be produced in the melts. For example, polysulfide ions were produced metastably by imposing a reduced sulfur atmosphere on an oxidized sulfur-free melt. This leads to potentially unique colorings of glass via this process; and in addition, may explain in part some of the problems associated with changing a commercial melter from flint (oxidized sulfur) glass production to amber (reduced sulfur) glass production or by unintentional changes in the redox state of the melt [23]. This may be significant in the processing of nuclear waste in glass melts, since often times an oxidized melt is being imposed in more reducing conditions due to processing constraints; however, this transient sulfur species may also be negated by mutual interactions with other redox species that may be present in the melt, most notably iron.

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6. References

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