# Kinetic Analysis of NaF Vaporization in SiF$_4$-Ar Mixture

YOSHIAKI KASHIWAYA and ALAN W. CRAMB

Slags used in steelmaking and continuous casting that contain SiO$_2$, Na$_2$O, and CaF$_2$ tend to be unstable and gaseous. Species, such as NaF and SiF$_4$, evolve simultaneously from these slags at steelmaking temperatures. In addition, the reaction between NaF and SiF$_4$ can occur to produce Na$_2$SiF$_6$ (sodium hexafluorosilicate). In a previous study on the vaporization of NaF into an inert gas stream, the diffusivity of NaF in argon, nitrogen, and helium was measured. In this study, the rate of NaF vaporization in a SiF$_4$ atmosphere was measured. Ternary diffusion coefficients were then evaluated from the binary diffusion coefficients obtained in a previous study, and a kinetic analysis was carried out. The rate calculations were found to be in accord with the measured results, indicating that the experiments were carried out in a regime where diffusion of NaF from the surface of the sample was rate controlling.
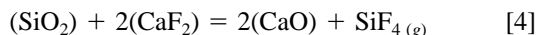
I. INTRODUCTION

FLUORIDE vaporization from slags containing CaF$_2$ is a serious problem in metallurgical industries in the continuous casting of steels, particularly where, in the secondary cooling chamber of a continuous caster, enhanced corrosion of the machine structure is found. The chemistry and physiochemical properties of slags can also vary as a function of time during processing due to vaporization of fluorides leading to process inconsistency and environmental problems. There are many types of gaseous fluorides that are stable at steel casting temperatures. NaF, SiF$_4$, AlF$_3$, and KF are stable under the conditions found in the mold of a continuous caster and can evolve from a mold slag into the surrounding atmosphere. In humid conditions, all of these fluorides would spontaneously form HF in contact with water and/or water vapor, as shown in Eqs. [1] through [3].

$$2NaF + H_2O = Na_2O + 2HF \qquad [1]$$

$$SiF_4 + 2H_2O = SiO_2 + 4HF \qquad [2]$$

$$CaF_2 + H_2O = CaO + 2HF \qquad [3]$$
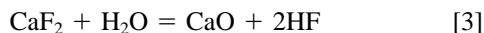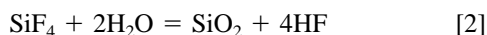
In the case of slag containing Al$_2$O$_3$ and K$_2$O, more complicated formation reactions of fluorides will also occur.[1]

SiF$_4$ can also vaporize from a slag containing SiO$_2$ and CaF$_2$, and this reaction is expressed in Eq. [4]. The vaporization kinetics of SiF$_4$ from several types of slags were recently studied,[1–4] as SiF$_4$ is a stable gas from ambient to high temperatures. However, when a slag contains Na$_2$O, SiO$_2$, and CaF$_2$, the vaporization species consist of not only SiF$_4$ but also NaF. Furthermore, as NaF deposits at moderate temperatures ($<$1273 K), precipitation of NaF on cooled surfaces can be a problem.

The reactions for SiF$_4$ and NaF vaporization are as follows:

$$(SiO_2) + 2(CaF_2) = 2(CaO) + SiF_{4\,(g)} \qquad [4]$$

$$(Na_2O) + (CaF_2) = (CaO) + 2NaF_{(g)} \qquad [5]$$

When SiF$_4$ and NaF vaporize simultaneously, the reaction between SiF$_4$ and NaF can produce sodium hexafluorosilicate (Na$_2$SiF$_6$), as shown in Eq. [6]. It is important to understand the behavior of Na$_2$SiF$_6$ during the vaporization of SiF$_4$ and NaF and to determine its effect on the vaporization kinetics of both species.

$$SiF_{4(g)} + 2NaF_{(l;g)} = Na_2SiF_{6\,(s)} \qquad [6]$$

Figure 1 shows the pseudobinary phase diagram in a NaF-SiF$_4$ system.[5,6,7] The phase diagram was obtained by differential thermal analysis using a sealed tantalum capsule, as the dissociation pressure of Na$_2$SiF$_6$ exceeds 70 atm at 1173 K. The diagram is not valid at 1 atmosphere total pressure as SiF$_4$ is gaseous, however, Na$_2$SiF$_6$ can exist at 1 atm when SiF$_4$ exists continuously in the atmosphere. The free energy of Reaction [6] in the solid state of Na$_2$SiF$_6$ was measured by Chiotti[7] and the free energy of a homogeneous solution of NaF-Na$_2$SiF$_6$ will be developed in a subsequent article.[11]

In this study, vaporization of NaF in a SiF$_4$-Ar gas mixture was measured, and the effect of the interaction of NaF and SiF$_4$ on the vaporization rate was investigated. The experimental technique was developed by the authors[8] in a previous study, where the vaporization of NaF in argon was measured.

II. EXPERIMENTAL

Figure 2 shows a schematic of the experimental apparatus. The weight change of NaF in SiF$_4$ gas was measured by thermogravimetric analysis. Reagent grade NaF was used for the experiments.

The crucible was made of platinum and had a 12 mm inner diameter and a 14 mm depth. The reaction tube (38-mm i.d. and 50-cm length) was made of mullite and connected to a PYREX* joint attached to the electronic balance. In every

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*PYREX is a trademark of Corning Glass Works, Corning, NY.

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experiment, the gas system was evacuated by a vacuum pump and checked for gas leakage before the experiment was initiated. Since the SiF$_4$ gas is potentially hazardous,
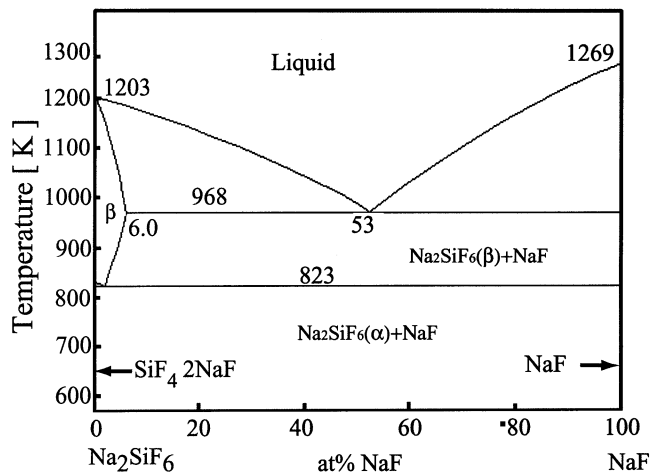
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Manuscript submitted September 22, 2000.

Fig. 1—Psuedobinary diagram of NaF-SiF$_4$.[5,6,7]

Fig. 2—Experimental apparatus.

Fig. 3—Treatment method for SiF$_4$ in exhaust.

Fig. 4—Typical curve of sample weight change and classification of reaction mechanism in the reaction curve.
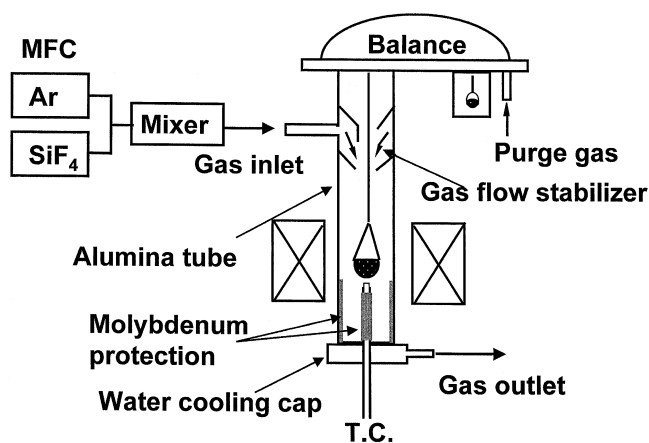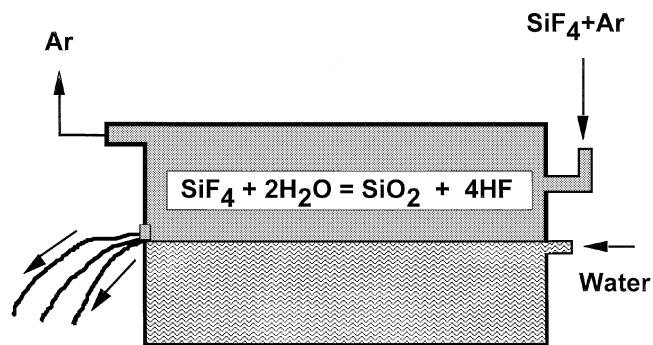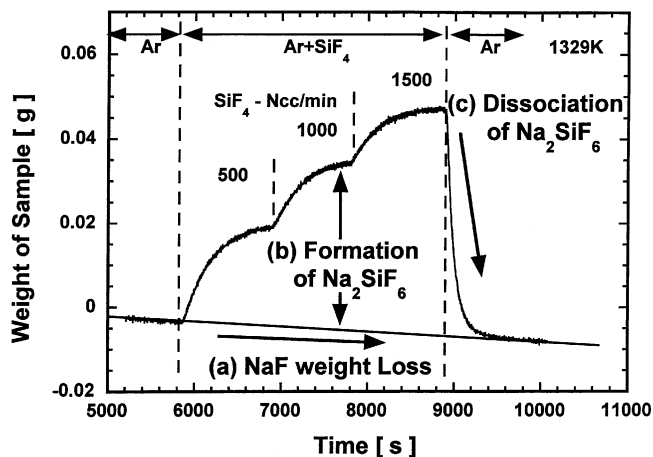
care was taken to avoid gas leakage and to render the exhaust gas harmless.

As NaF vapor deposits around 1273 K, a reaction between Al$_2$O$_3$ and NaF can occur inside the reaction tube. The inside of the reaction tube was, therefore, covered by molybdenum sheets to prevent this reaction. Argon and SiF$_4$ gas were controlled by a mass flow controller, and the gas mixture was introduced to the reaction tube through a gas mixer. A gas flow stabilizer[8] was utilized to reduce turbulence and minimize measurement error (Appendix).

Since diffusivity is sensitive to the reaction temperature, a naked B-type thermocouple was inserted into the reaction tube. The distance between the tip of the thermocouple and the bottom of the crucible was 2 mm to ensure that the thermocouple did not disturb the movement of the crucible during weight loss.

Figure 3 shows the method of SiF$_4$ removal from the exhaust gas. SiF$_4$ reacts with H$_2$O, and the products are HF and SiO$_2$ (Eq. [1]). It is also important to remove the SiO$_2$ formed on the surface of water, as SiO$_2$ can clog the system and decrease the reaction efficiency.

The temperature range of the experiment was from 1273 to 1673 K, and the flow rate of SiF$_4$ was varied from 500 to 1500 Ncc/min.

III. RESULTS AND DISCUSSION

The rate of vaporization of NaF was measured in a SiF$_4$ gas atmosphere. Reagent grade NaF was placed in a platinum crucible and heated in a flowing Ar gas atmosphere (500 Ncc/min). SiF$_4$ gas from a cylinder was then added to the Ar gas at the desired temperature (1273 to 1700 K), and the flowrate of SiF$_4$ gas was changed stepwise from 500 to 1500 Ncc/min at each experimental temperature. The typical weight change of the sample is shown in Figure 4 (1329 K).

If SiF$_4$ gas was not introduced to the reaction tube, the weight of NaF decreased constantly with time by vaporization of NaF. When SiF$_4$ gas was added to the argon, the weight of NaF increased rapidly and reached a steady-state weight. The weight at steady state varied with the flowrate of SiF$_4$. This weight gain, caused by the reaction between SiF$_4$ and NaF, is explained by Eq. [6] and was due to the formation of Na$_2$SiF$_6$. When the SiF$_4$ was turned off, the weight of the sample drastically decreased. Hence, Figure 4 contains the three phenomena.

(a) The slope of the baseline corresponds to the vaporization of NaF.
(b) The increase of the sample weight corresponds to the formation of Na$_2$SiF$_6$.
(c) The rapid decrease of the sample weight from turning off the SiF$_4$ corresponds to the dissociation of Na$_2$SiF$_6$.

As mentioned previously, the vaporization of NaF (a) was

studied in this article. The concentration of Na_2SiF_6 formed during the experiment was a maximum of 1.5 mol pct and was generally less than 1 mol pct. It was found that the existence of Na_2SiF_6 did not affect the vaporization of NaF in this concentration range of Na_2SiF_6 (Figure 1).

A. Ternary Diffusion in NaF-SiF4-Ar System

Binary diffusion of *i*-gas in *j*-gas is generally described by Fick's law:

$$-J_i = De_{ij} \cdot \nabla C_i \qquad [7]$$

where De_{ij} means the diffusion coefficient in a binary system.

In the case of *n*-component system, the multicomponent diffusion is described by Onsager.[9] The flux of *i*-gas, J_i, is expressed by the multicomponent diffusion coefficient, D_{ij}, and concentration gradient of the gases except solvent gas.

$$-J_i = \sum_{j=1}^{n-1} D_{ij} \cdot \nabla C_j \qquad [8]$$

Then, the ternary diffusion in a NaF-SiF4-Ar system in one dimension is expressed as follows:

$$-J_1 = D_{11} \cdot \frac{\partial}{\partial z} C_1 + D_{12} \cdot \frac{\partial}{\partial z} C_2 \qquad [9]$$

$$-J_2 = D_{21} \cdot \frac{\partial}{\partial z} C_1 + D_{22} \cdot \frac{\partial}{\partial z} C_2 \qquad [10]$$

where C_1 and C_2 denote the concentration of NaF and SiF_4, respectively. D_{11} and D_{12} are multicomponent diffusion coefficients (ternary diffusion coefficients) for the diffusion of NaF, and also D_{21} and D_{22} are the ternary diffusion coefficients of SiF_4. The relationship between the ternary diffusion coefficient (D_{ij}) and the binary diffusion coefficient (De_{ij}) was given by Cussler:[10]

$$D_{11} = \left[\frac{\dfrac{x_1}{De_{12}} + \dfrac{x_2 + x_3}{De_{23}}}{\dfrac{x_1}{De_{12}De_{13}} + \dfrac{x_2}{De_{12}De_{23}} + \dfrac{x_3}{De_{13}De_{23}}} \right] \qquad [11]$$

$$D_{12} = \left[\frac{x_1\left(\dfrac{1}{De_{13}} - \dfrac{1}{De_{12}}\right)}{\dfrac{x_1}{De_{12}De_{13}} + \dfrac{x_2}{De_{12}De_{23}} + \dfrac{x_3}{De_{13}De_{23}}} \right] \qquad [12]$$

$$D_{21} = \left[\frac{x_2\left(\dfrac{1}{De_{23}} - \dfrac{1}{De_{12}}\right)}{\dfrac{x_1}{De_{12}De_{13}} + \dfrac{x_2}{De_{12}De_{23}} + \dfrac{x_3}{De_{13}De_{23}}} \right] \qquad [13]$$

$$D_{22} = \left[\frac{\dfrac{x_1 + x_3}{De_{13}} + \dfrac{x_2}{De_{12}}}{\dfrac{x_1}{De_{12}De_{13}} + \dfrac{x_2}{De_{12}De_{23}} + \dfrac{x_3}{De_{13}De_{23}}} \right] \qquad [14]$$

where the subscripts 1, 2, and 3 denote NaF, SiF_4, and Ar in the binary system (right-hand side), respectively. In the ternary system, the diffusion coefficients are not symmetric, $D_{12} \neq D_{21}$. The ternary diffusion coefficient, D_{11} and D_{22},
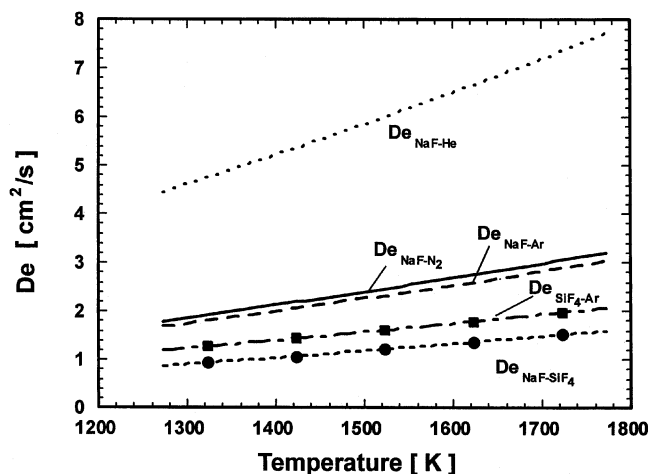

Fig. 5—Comparison of binary diffusion coefficient among NaF, SiF4, and Ar.

Table I. Binary diffusion coefficient calculated

Temp. K	De_{NaF-Ar} (cm^2/s)	$De_{NaF-SiF4}$ (cm^2/s)	$De_{SiF4-Ar}$ (cm^2/s)
1473	2.1879	1.1426	1.5233
1573	2.4577	1.2884	1.6989
1673	2.7394	1.4410	1.8819
1773	3.0326	1.6001	2.0721

are called the main term and have almost the same magnitude as the binary diffusion coefficient. On the other hand, the cross term, D_{12} and D_{21}, are less than 20 pct of the main term. In other words, D_{11} is a diffusion coefficient of NaF, and D_{12} is an effect of SiF_4 on the NaF diffusion. Also, D_{22} is a diffusion coefficient of SiF_4, and D_{21} is an effect of NaF on the SiF_4 diffusion.

Figure 5 shows the comparison of the binary diffusion coefficient calculated by the Chapman–Enskog equation, in which the parameters, such as collision diameter and collision integral, were obtained in the previous study.[8] The diffusion coefficient in the NaF-SiF4 system, $De_{NaF-SiF4}$, is lowest due to the large molecular weight of SiF_4 (104) and the large collision diameter (4.88 Å). The value in SiF_4-Ar system, $De_{SiF4-Ar}$, is between the NaF-Ar and SiF_4-NaF system. An example of the calculation result for the binary system used in this study is shown in Table I.

Using these calculated binary diffusion coefficients (Figure 5), the ternary diffusion coefficients were evaluated under several conditions. Figure 6 shows the temperature variation during the experiment, when the flowrate of SiF_4 was changed from 500 to 1500 Ncc/min in three steps. It was found that the temperature of the sample decreased with an increase of SiF_4 gas flowrate. Since the diffusion of gas is strongly affected by temperature, these temperature variations were taken into account in the calculation.

Figures 7 and 8 show the results of the calculation for the ternary diffusion coefficients during an experiment at 1344 K. The binary diffusion coefficients (De_{NaF-Ar}, $De_{SiF4-Ar}$, and $De_{NaF-SiF4}$) were also plotted for comparison. Figure 7 shows the ternary diffusion coefficients (D_{11} and D_{12}) related to NaF. The main term of NaF diffusion, D_{11},
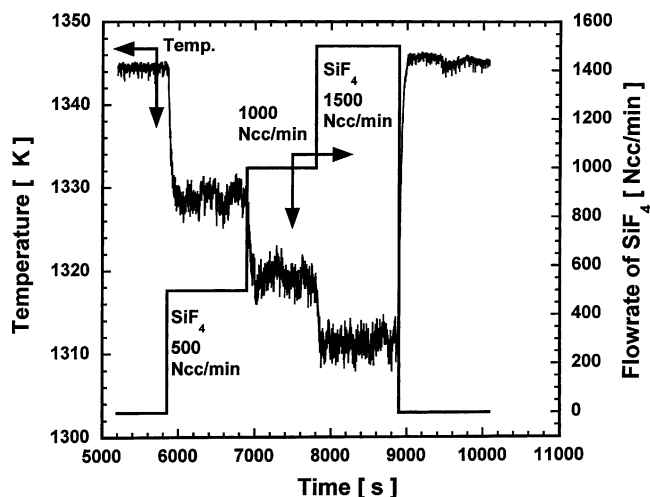
Fig. 6—Temperature variation of sample during experiment.

Fig. 9—Illustration of calculation model for NaF diffusion in SiF$_4$-Ar mixture.
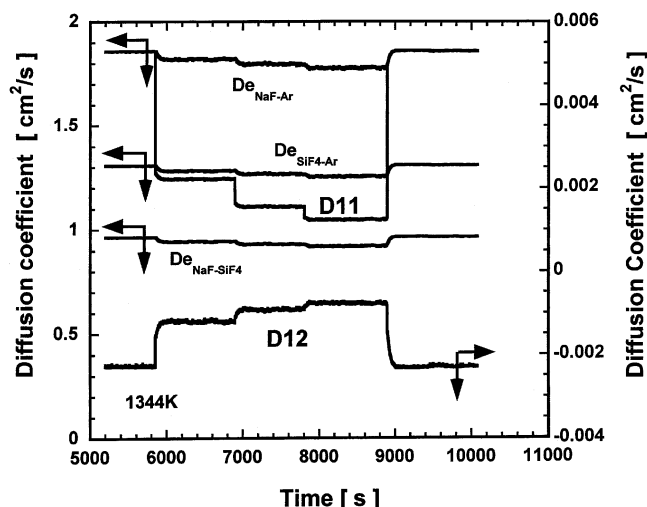

Fig. 7—Variation of the ternary diffusion coefficient related to NaF during experiment.
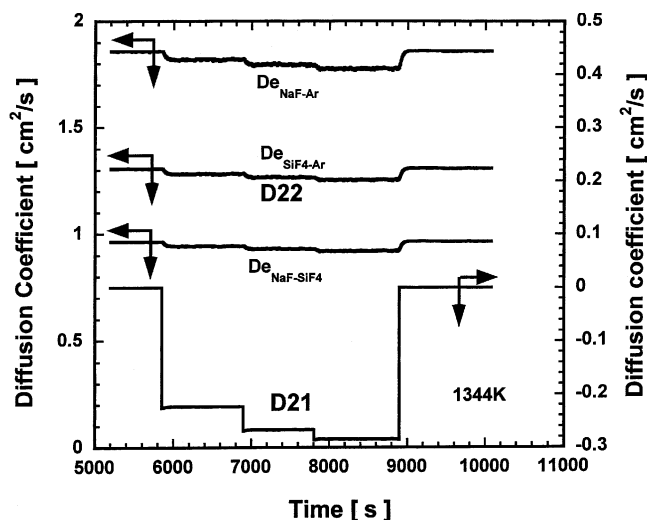
Fig. 8—Variation of the ternary diffusion coefficient related to SiF$_4$ during experiment.
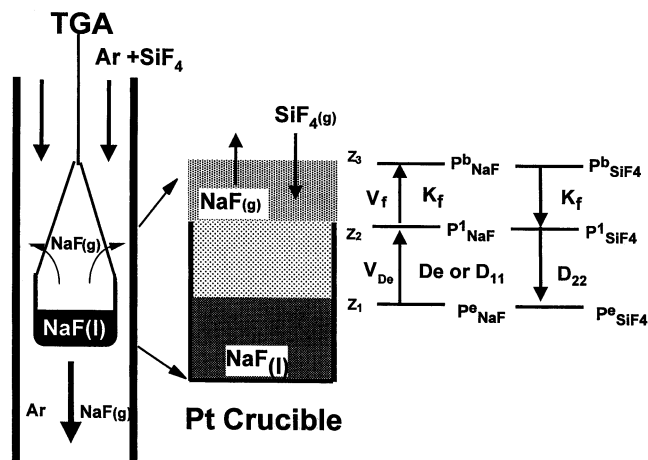
decreased with the addition of SiF$_4$, from that of NaF-Ar system to that of the SiF$_4$-NaF system. The absolute value of the cross term, D_{12}, decreased with the increase of SiF$_4$, however, the value was negative and small (about 0.001 cm^2/s).

Figure 8 shows the variation of the ternary diffusion coefficient of SiF$_4$ at 1344 K. The main term, D_{22}, was almost the same as the binary diffusion coefficient in the SiF$_4$-Ar system ($De_{\text{SiF4-Ar}}$). The value of the cross term was relatively large and about 16 pct at 500 Ncc/min and 20 pct at 1500 Ncc/min corresponding to D_{22}. These ternary diffusion coefficients were used for estimation of the NaF vaporization from the platinum crucible in the SiF$_4$-Ar mixture. The calculation results of the ternary diffusion coefficients are shown in Table II for two gas conditions.

B. Estimation of NaF Vaporization in SiF$_4$-Ar Mixture

As mentioned above, the baseline of the weight-change curve corresponds to the NaF vaporization (Figure 4). In this section, the vaporization of NaF was calculated for several experiments using the ternary diffusion coefficient obtained in the present study. The calculation was carried out using Eq. [15], and the model for calculation was shown in Figure 9. As the flow rate is high enough to neglect the mass transfer ($1/kf \rightarrow 0$) and D_{12} can be neglected by the reason mentioned above, the diffusion coefficient, De, equals D_{11}. Thus, Eq. [15] can be modified to Eq. [16].

$$V_{\text{NaF}} = \frac{-2\pi r^2}{(1/k_f + \Delta z/De)} (P^e_{\text{NaF}} - P^b_{\text{NaF}})/\,\text{R}T \qquad [15]$$

$$V_{\text{NaF}} = \frac{-2\pi r^2 D_{11}}{\Delta z} (P^e_{\text{NaF}} - P^b_{\text{NaF}})/\,\text{R}T \qquad [16]$$

An equilibrium vapor pressure of NaF P^e_{NaF} was evaluated by the same method, and a distance of diffusion, Δz, was calculated using the density of NaF melt, as described in a previous article.[8] It was assumed that the precipitation of Na$_2$SiF$_6$ did not affect the vaporization kinetics of NaF. The distance from the surface of molten NaF to the top of the crucible, z, was changed from 7 to 10 mm during the experiment due to vaporization. In this study, we ascertained the validity of Eq. [16] from the following two points.

Table II. Calculation examples for the ternary diffusion coefficient

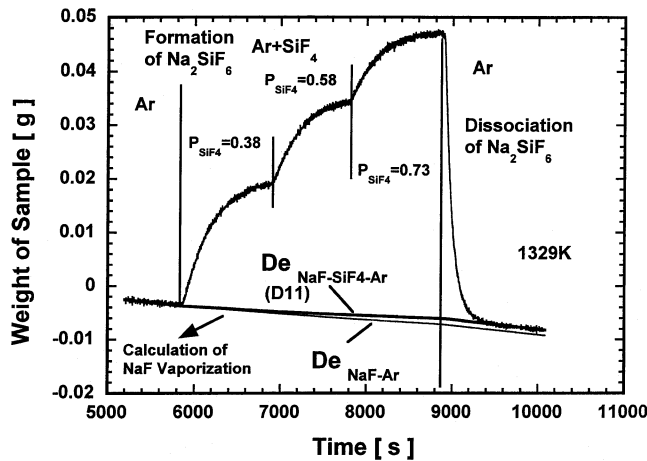| Temp. K	$x_{NaF} = 0.0544$, $x_{SiF4} = 0.7092$, $x_{Ar} = 0.2364$				$x_{NaF} = 0.2152$, $x_{SiF4} = 0.5886$, $x_{Ar} = 0.1962$			
	D_{11}	D_{12}	D_{22}	D_{21}	D_{12}	D_{12}	D_{22}	D_{21}
1473	1.3360	-0.0455	1.5064	-0.3101	1.4588	-0.1862	1.4551	-0.2665
1573	1.5050	-0.0505	1.6808	-0.3343	1.6382	-0.2070	1.6259	-0.2875
1673	1.6817	-0.0557	1.8625	-0.3589	1.8288	-0.2285	1.8038	-0.3090
1773	1.8659	-0.0611	2.0515	-0.3842	2.0273	-0.2593	1.9889	-0.3311

Fig. 10—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1329 K.
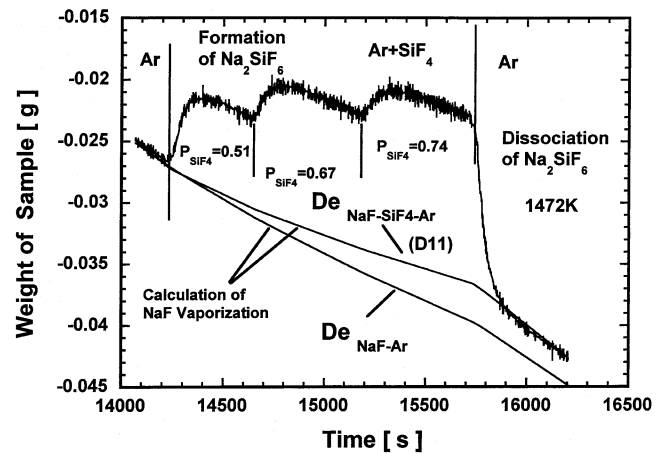

Fig. 12—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1472 K.
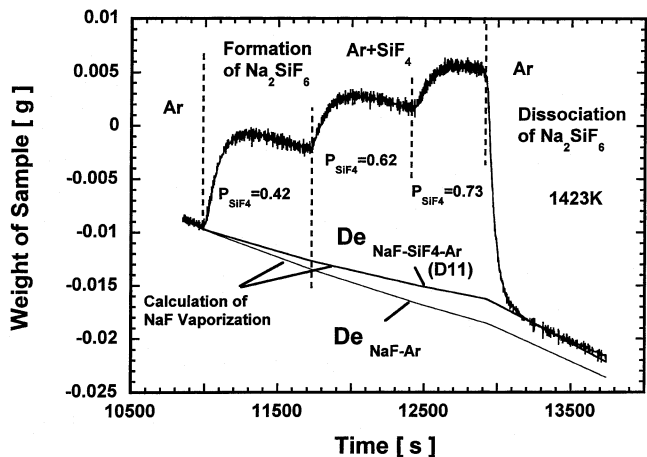

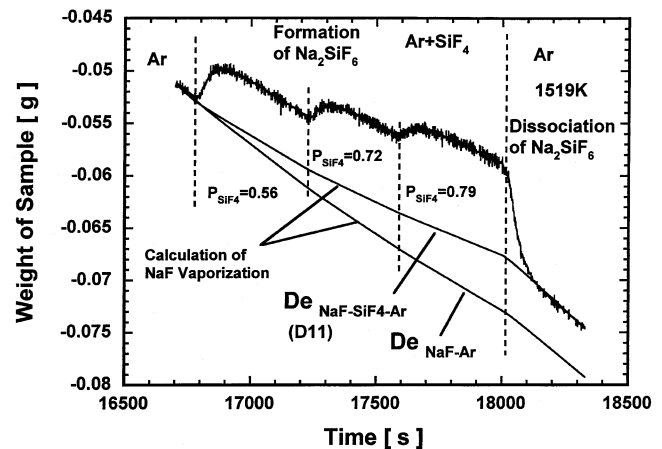Fig. 11—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1423 K.

Fig. 13—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1519 K.

(1) The gas flow around the crucible should be stable. If the gas flow was turbulent, the vibration of the crucible would increase and lead to agitation of the surface of melt. We developed the gas stabilizer shown in Figure 2 to counter this problem. The influence of the stabilizer is shown in the Appendix (Figure A1). A stable gas flow was established to allow stable diffusion from the surface of melt to the top of the crucible.

(2) If the gas flowed into the crucible, the diffusion coefficient obtained by analysis would be very large. However, the obtained values were reasonable[8] and can be predicted by Chapman–Enskog theory.

If the rate of surface vaporization is not rapid, the actual vapor pressure P^{e-a}_{NaF} at the NaF melt surface is lower than the equilibrium vapor pressure P^{e}_{NaF} (in Eq. [16], ($P^{e-a}_{NaF} < P^{e}_{NaF}$)). In this situation, the obtained diffusion coefficient will be larger than the inherent value, and the temperature dependence will not be predicted by Chapman–Enskog theory. Furthermore, in a previous study,[8] we measured the diffusion coefficients in NaF-Ar, NaF-N$_2$, and NaF-He systems. In the case of the rate of controlling step being surface vaporization, the difference among three diffusion coefficients should be almost zero or very small. However, this was not found to be true. We concluded that it would be reasonable to define the vapor pressure at surface of NaF
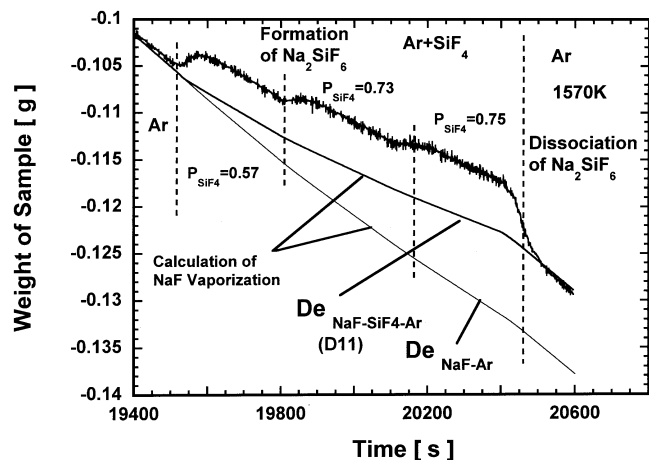
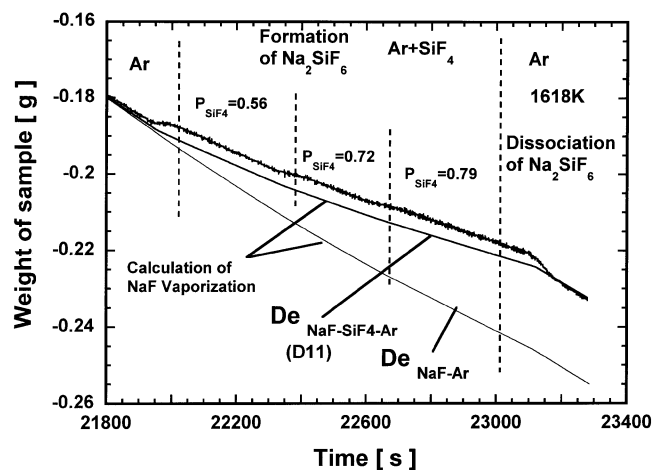Fig. 14—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1507 K.

Fig. 16—Result of calculation, from which was subtracted the effect of NaF vaporization (1329 K).

Fig. 15—Comparison of base lines calculated using ternary and binary diffusion coefficients at 1618 K.
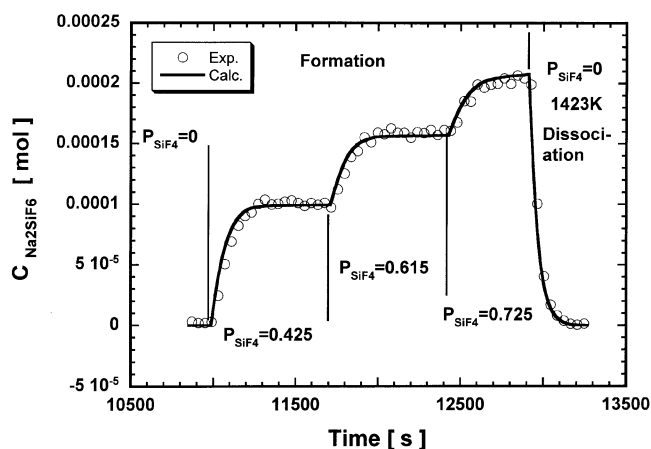
Fig. 17—Result of calculation, from which was subtracted the effect of NaF vaporization (1423 K).

melt to be equal to its equilibrium vapor pressure. One possibility exists to decrease the vapor pressure at surface—the precipitation of a substance at the surface of the melt that inhibits vaporization. However, at the experimental temperature (> 1329 K), which is above the melting temperature (1269 K), and using highly pure starting materials, where impurities can not be detected by ICP, it is doubtful if precipitation of unwanted phases is problematic.

Figures 10 through 15 are the comparison between the calculation and the observation at 1329, 1423, 1472, 1519, 1570, and 1618 K, respectively. The results of the calculation using the binary diffusion coefficient, De_{NaF-Ar}, could not explain the baseline, especially at high temperature because of the high vapor pressure of NaF. The discrepancies between the ternary diffusion coefficient (D_{11}) and binary one (De_{NaF-Ar}) increased with temperature. The calculation results using the ternary diffusion coefficients were in good agreement with the observations after the evaporation of Na_2SiF_6.

In Figure 10, the slope of the baseline was not large because the temperature was relatively close to the melting point of NaF and the vapor pressure was low. In the case of the formation of Na_2SiF_6, the amount of Na_2SiF_6 formation was highest at low temperatures and decreased with
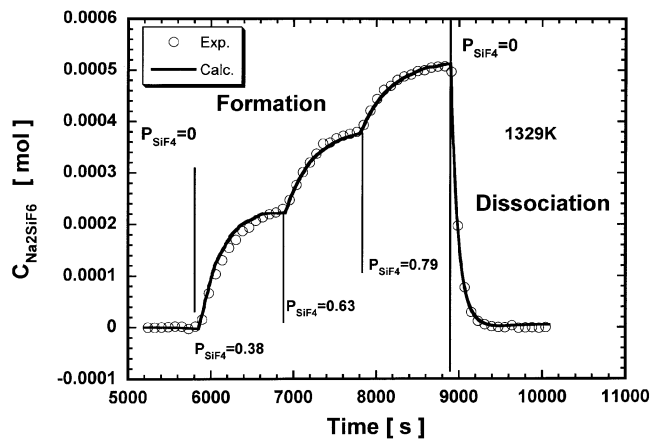
increasing temperature, which means that the Na_2SiF_6 is not as stable at higher temperatures. The amount of NaF vaporization was subtracted from data measured, then, the baseline became parallel to the x-axis. Two examples of this calculation are shown in Figures 16 and 17.

From these results, it can be shown that the binary diffusion coefficients obtained in the previous study can be used to estimate the ternary diffusion coefficients and explain the vaporization kinetics of NaF in complex gas mixture. Furthermore, it was found that the formation and dissociation of Na_2SiF_6 does not affect the vaporization of NaF.

IV. CONCLUSIONS

The vaporization rate of NaF in a SiF_4-Ar system was measured. Ternary diffusion coefficients were then evaluated from the binary diffusion coefficients obtained in a previous study, and a kinetic analysis was carried out. The rate calculations were found to be in accord with the measured results, indicating that the experiments were carried out in a regime where the diffusion of NaF from the surface of the sample was rate controlling.
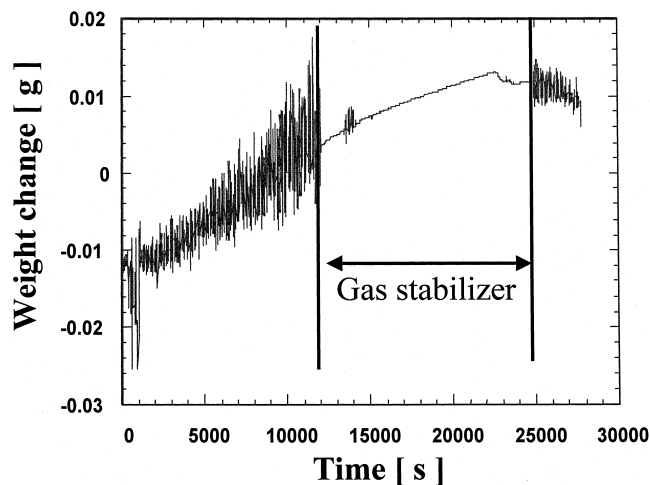
Fig. A1—Influence of gas stabilizer on the measurement of weight gain of NaF.

APPENDIX

Figure A1 shows the influence of a gas stabilizer (Figure 2) on the measurement of weight change. The temperature was 1329 K and the gas composition was Ar-40 pct SiF_4 (total 1000 Ncc/min). The gas was introduced to the reaction tube before and after the stabilizer. Then, the influence of the gas stabilizer was examined. In Figure A1, the gas was introduced after the stabilizer, and quite a large vibration occurred on the crucible. The pass of gas flow was changed before the stabilizer from 12,000 seconds and quite a stable weight gain, caused by the formation reaction between NaF and SiF_4, was obtained. There is some noise at 15,000 seconds which resulted from hand touching. In the present study, quite a stable gas flow can be obtained using a gas stabilizer, which attained the stable measurement of the diffusion coefficient.

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