Effect of $^{235}\text{UF}_6-^{238}\text{UF}_6$ Gas Mixing on the Kinetic Rate of the Isotope Exchange Reaction between $^{235}$U-Enriched UF$_5$ Nanoparticles and Natural UF$_6$ Gas

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The isotope exchange reaction between $^{235}$U-enriched UF$_5$ nanoparticles and natural UF$_6$ gas,

$$^{235}\text{UF}_5(\text{solid}) + ^{238}\text{UF}_6(\text{gas}) \leftrightarrow ^{235}\text{UF}_6(\text{gas}) + ^{238}\text{UF}_5(\text{solid})$$

(1)

is important for the development of the molecular laser isotope separation of uranium (abbreviated as MLIS), since this reaction reduces the enrichment of $^{235}$U in MLIS.

Grigor'ev and co-workers(1) were the first to report for this isotope exchange reaction under a static condition. Recently, Onoe and co-workers(2) demonstrated that this reaction proceeds with two kinetic rates. More recently, Yato and co-workers(3)(4) proposed a kinetic model for this reaction and estimated the kinetic constants of the two rates. Unfortunately, Grigor'ev and co-workers did not describe the details of the experimental conditions used in their work(1). In all other studies(2)-(4), a large cell about 16,000 cm$^3$ in volume was used. In such a large cell, it takes considerable time to achieve isotopically complete mixing between $^{235}$UF$_6$ and $^{238}$UF$_6$ gases under a static condition, and it is still unclear whether or not the $^{235}$UF$_6-^{238}$UF$_6$ gas mixing in bulk affects the rate of the isotope exchange reaction shown in Eq.(1). Therefore previously reported(1)-(4) rates of Eq.(1) may include not only the intrinsic rate of Eq.(1) but also the effect of the gas mixing rate. In the previous studies(1)-(4), however, no attention was paid to this gas-mixing effect. The aim of the present work is to examine the effect of the gas mixing on the kinetic rate of the isotope exchange reaction.

1. Experimental

In order to minimize the effect of the isotopic gas mixing and local inhomogeneity in the gas phase of $^{235}$UF$_6$ and $^{238}$UF$_6$ on the kinetic rate of Eq.(1), we used a stainless steel cell with a small volume of 383 cm$^3$ (10 cm in diameter). Figure 1 shows schematic (a) side and (b) top views of the reaction cell. We used an impeller made of a nickel-coated soft-iron disc rotor with four stainless steel blades (8 cm in diameter and 2 cm in height) in order to achieve homogeneous mixing between $^{235}$UF$_6$ and $^{238}$UF$_6$ gases. This impeller was mounted on the top of the inside wall of the cell and its rotation rate was controlled in the range of 0 to 1,000 rpm by a magnetic rotor, as shown in Fig. 1. The cell was equipped with four CaF$_2$ windows. One pair of opposing windows was used for KrF laser irradiation, while the other pair was for UV spectroscopy to monitor the concentration of residual UF$_6$ gas in the cell. A shutter was used to prevent photoproduced UF$_5$ of the present work is to examine the effect of the gas mixing on the kinetic rate of the isotope exchange reaction.
particles from being deposited on the optical windows for UV spectroscopy. The cell was passivated with 20 Torr of ClF₃ to remove H₂O which might react with the UF₆ gas.

For the production of the UF₅ particles, 4 Torr of 7.03% ²³⁵U-enriched UF₆ and 20 Torr of CH₄ were introduced into the cell. Then, the gas mixture was irradiated with KrF laser (Lumonics EX-700, 248 nm; 36.4 mJ; 2Hz) pulses (9,600 shots). The CH₄ gas was used for scavenging fluorine radicals produced from photo-irradiated UF₆. Complete decomposition of the UF₆ gas was confirmed by UV spectroscopy (Shimadzu UV-3100). Twenty-four hours after the irradiation, residual gases were evacuated carefully in order not to eliminate the UF₅ particles from the cell. Then, natural UF₆ gas at a pressure of 4 Torr or 12 Torr was introduced into the cell. During the isotope exchange reaction, the gas mixture was stirred by the impeller at various rotation rates such as 0, 180, 500, and 1,000 rpm. After an isotope exchange reaction time of 60 min or 120 min, all UF₆ gas was transferred from the cell to a sample tube cooled with liquid nitrogen, and the isotopic fraction, ²³⁵U/(²³⁵U+²³⁸U), of the sampled UF₅ gas was measured using a magnetic-sector mass spectrometer. During the isotope exchange reaction, the amount of UF₆ decomposed or adsorbed on the inside wall of the cell was less than 5% of the initial amount of UF₆ gas. We call this experiment the "small cell experiment" (abbreviated SCE).

The details of experiments using a large cell about 16,800 cm³ in volume (25 cm in diameter and 29.5 cm in height) have been described elsewhere. During the isotope exchange reaction, the gas mixture was stirred by an impeller (13 cm in diameter and 2.4 cm in width) mounted at the top of the inside wall of the chamber. The impeller was rotated at rates in the range from 0 to 100 rpm. This experiment is called the "large cell experiment" (abbreviated LCE).

The isotopic fraction, ²³⁵U/(²³⁵U+²³⁸U), of the sampled UF₅ gas was measured with a magnetic-sector mass spectrometer (Finigan MAT-271 for SCE and MAT-281 for LCE). The measurement accuracy of the isotopic fraction was 5x10⁻⁵% for the MAT-271, while it was 2x10⁻³% for the MAT-271. In the both cases of SCE and LCE, the reproducibility of the isotopic fraction of the sampled UF₅ gas in the experiments performed under the same conditions were less than 4x10⁻³%.

2. Results and Discussion

First, we examined the effect of the ²³⁵UF₆-²³⁸UF₆ gas mixing on the kinetic rate of the isotope exchange reaction between 150 mg of 7.03% ²³⁵U-enriched UF₅ particles and 7 Torr (2,250 mg) of natural UF₆ gas for LCE. Figure 2 shows the time evolution of the isotopic fraction of the UF₅ gas for moderate rotation rates (0, 50, 100 rpm) of the impeller. It was found that the isotope exchange reaction described by Eq.(1) was affected by the rotation rate. This indicates that the reaction rate obtained for LCE reflects the intrinsic kinetic rate of Eq.(1) under the influence of the ²³⁵UF₆-²³⁸UF₆ gas-mixing. Since the previous results were obtained using a similar large cell, it is likely that those results were also affected by the gas mixing. Accordingly, the intrinsic reaction rate of Eq.(1) has not been determined accurately until now.

We next examined the effect of the gas mixing on the kinetic rate of Eq.(1) for SCE. Figure 3 shows the dependence of the isotopic fraction of the UF₅ gas on the impeller rotation rate under two experimental conditions: (a) 4 Torr (30 mg) of natural UF₆ gas, 28 mg of 7.03% ²³⁵U-enriched UF₅ particles, and a sampling time of 60 min and (b) 12 Torr (90 mg) of natural UF₆ gas, 28 mg of 7.03% ²³⁵U-enriched UF₅ particles, and a sampling time of 120 min. Under condition (a), the isotopic fraction of the UF₅ gas was independent of the impeller rotation rate in the range of 0 to 100 rpm. This indicates that the effect of the ²³⁵UF₆-²³⁸UF₆ gas mixing on the rate of Eq.(1) is negligible under this condition. On the other hand, under condition (b), the isotopic fraction of the UF₅ gas depended on the rotation rate in the range below 450 rpm and was independent of the rotation rate in the range above this value. In this case, it was found that the gas-mixing effect can be neglected for impeller rotation rates higher than 450 rpm.

Let us consider why the gas-mixing effect appeared under condition (b). Since the self-diffusion coefficient of UF₆ molecules under condition (b) is 1/3 of that under condition (a), the diffusion rate of ²³⁵UF₆ molecules among ²³⁸UF₆ molecules under condition (b) is small, resulting in a small rate of the apparent isotope exchange reaction at impeller rotation rates lower than 450 rpm. For this reason, a rotation rate higher than 450 rpm was necessary to achieve the gas-mixing-
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Free (or complete mixing) condition in the experiment under condition (b). Similarly, the self-diffusion coefficient for 7 Torr UF6 gas is about half of that for 4 Torr. A rotation rate higher than 200 rpm might be necessary to achieve the gas-mixing-free condition even for SCE. In the previous studies (2)-(4), the UF5 nanoparticles produced by photodissociation of UF6 were typically about 10-15 nm in diameter and formed three-dimensional network structures (6)-(8). In general, the apparent reaction rate of fluorine atom exchange on the surface of these nanoparticles includes not only the intrinsic surface exchange rate but also (A) the isotopically incomplete mixing in the bulk UF6 gas phase, (B) the diffusion of the UF6 gas inside the three-dimensional network structure, and (C) the mass transfer of UF6 from the bulk gas phase to the network structure.

Since we do not know the exact flow pattern of the batch reaction cell with or without an impeller, quantitative discussion is difficult. Nevertheless, it is reasonable to assume that case (b) at 12 Torr requires gas-mixing above 450 rpm, while gas mixing is not necessary at 4 Torr in case (a). In a previous paper on laser isotope separation of tritium, Takeuchi and co-authors (9) confirmed that the gas mixing was not necessary to achieve uniform isotopic compounds in a small cell (30 cm in length, 2 cm in diameter) at 200 Torr. The only reliable way to avoid the effect of isotopically imperfect mixing in the gas phase on the apparent rate of Eq. (1), in a batch reaction experiment is to obtain the results under the conditions such as these in Figs. 3(a) and (b). In those cases, the effect of (A) was negligible in determining the intrinsic isotope exchange reaction rate of Eq. (1). Using the small cell under the gas-mixing-free condition, we have confirmed that the reaction described by Eq. (1) involves two rate processes (10). The reaction mechanism behind the two rate processes and the negligibility of the effects (B) and (C) on the intrinsic isotope exchange reaction rate are now under investigation.

The effect of 235UF6-238UF6 gas mixing on the isotope exchange reaction was examined by changing the cell size and the rotation rate of an impeller. This effect was found to be significant in the intrinsic kinetic rate of the isotope exchange reaction in a large cell. This indicates that the previously reported kinetic rate of the isotope exchange reaction does not necessarily correspond to the intrinsic rate. The present results obtained using a small cell equipped with an impeller under the gas-mixing-free condition enable determination of the intrinsic kinetic rate of the isotope exchange reaction between 235U-enriched UF5 nanoparticles and natural UF6 gas.

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