A New Calculation Method for Simulation of the Growing Particles-Gas Reaction System

Jun ONOE, Yoshikazu KUGA and Kazuo TAKEUCHI

The Institute of Physical and Chemical Research (RIKEN)

2-1, Hirosawa, Wako-shi, Saitama-Pref. 351-01, Japan

Received December 4, 1991

The growing particles-gas reaction is very important in the molecular laser isotope separation of uranium-235 (^{235}U) at RIKEN, because an isotope exchange reaction between growing ^{235}U enriched UF_5 particles and natural UF_6 is thought to be one of the most serious problems which causes the separation factor to deteriorate. We present here a new simple calculation method to estimate the influence of this reaction system. Using an exchange reaction probability of 1.1×10^{-9} reported by G.Y. Grigorev et al., we found that the influence of the isotope exchange reaction between growing ^{235}U enriched UF_5 particles and natural UF_6 gas was negligible to the separation factor.

Key Words: growing particles, stop-go method, molecular laser isotope separation, isotope exchange reaction, separation factor, uranium-235(V) fluoride, uranium-238(V) fluoride

1. Introduction

In molecular laser isotope separation of ^{235}U at RIKEN (RIMLIS), the ν_3 vibrational mode (628 cm^{-1}) of supercooled $^{235}\text{UF}_6$ in a natural UF_6/Ar gas mixture is selectively excited and one of the U-F bondings is successively dissociated with a multi-frequency para- H_2 Raman laser to produce nonvolatile $^{235}\text{UF}_5$. The $^{235}\text{UF}_5$ molecules thus formed are immediately aggregated to form particles, which are collected onto an impaction plate¹⁾. The RIMLIS process is schematically shown in Fig. 1.

Grigorev and his coworkers first reported an isotope exchange reaction between ^{235}U -enriched UF_5 particles and natural UF_6 gas in a static cell²⁾. In this case, the isotope exchange reaction is expressed as;

According to their report, this reaction progressed with two rate processes: a fast rate process due to the exchange reaction between the outermost layer of the enriched

UF_5 particles and the natural UF_6 gas, and a slow one due to that between underlying layers of the UF_5 particles and the gas. The former was reported to be dominant up until 30 min, then the latter took over. By numerically fitting a calculated result to the experimental data, they estimated an exchange reaction probability of 1.1×10^{-9} , and a participation probability of the underlying layers in this exchange reaction of 0.6. We also have investigated the reaction shown in Eq. (1) between 7% ^{235}U -enriched UF_5 particles and natural UF_6 gas³⁾, and confirmed the progress of this reaction in a more rigorous manner. Namely, we used a dimensionless kinetic analysis of our experimental results to verify the two different rates, instead of the numerical fitting.

As shown in Fig. 1, the isotope exchange reaction is considered to occur not only between natural UF_6 gas and ^{235}U enriched UF_5 particles collected on the impaction plate (Process 2), but also between the UF_6 gas and growing ^{235}U enriched UF_5 particles

Fig. 1 Schematic representation of particle growth in the molecular laser isotope separation system for ^{235}U enrichment at RIKEN.

(Process 1). It seems from both the results reported by Grigorev et al. and the separate results by the authors that the influence of Process 2 is not negligible to the separation factor. Since the surface area of the UF_5 particles in Process 1 is much larger than that of Process 2, it is possible that the influence of Process 1 is more serious than that of Process 2, though the time scale of Process 1 is shorter than that of Process 2. Consequently, it is important to estimate the influence of this reaction against the separation factor of RIMLIS through Process 1.

In this paper, we present a new calculation method which is useful for simulation of such a growing particles-gas reaction, based on the kinetic experimental data reported by Grigorev et al..

2. Calculation Method

For the isotope exchange reaction between ^{235}U -enriched UF_5 particles and natural UF_6 gas in a static cell, Grigorev et al. derived kinetic equations as follows:

$$dL_5/dt = -k(L_5M_3 - L_3M_5) \quad (2)$$

$$dM_5/dt = k(L_5M_3 - L_3M_5) + f(a) \quad (3)$$

$$k = \delta^2 \omega v / 4V \quad (4)$$

where L_5 , L_3 , M_5 , and M_3 denote the number of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules, and that of $^{235}\text{UF}_5$ and $^{238}\text{UF}_5$ in the outermost layer of UF_5 particles, respectively. $f(a)$ is an additional term due to the exchange reaction between underlying layers of the UF_5 particles and UF_6 gas, and "a" denotes a participation probability of the underlying layers. k is a rate constant. δ , ω , v , and V represent an average distance (0.7 nm) between U atoms in $\beta\text{-UF}_5$ crystals, exchange reaction probability (1.1×10^{-9}), thermal velocity of UF_6 molecules, and cell volume, respectively.

For the growing UF_5 particles- UF_6 gas reaction, we simplified Process 1 as schematically shown in Fig. 2. Our calculation model is based on the following three assumptions. (1) Particle growth of UF_5 obeys Ulrich's model⁴⁾, which is simply but sufficiently useful to explain the particle growth for many cases⁵⁾. In this model shown in Fig. 2, the number of UF_5 molecules in a particle doubles for every collision, and the particle size remains the same until the next collision occurs. Namely, when S and P denote the numbers of UF_5 molecules in a particle and of collision between UF_5 particles, respec-

Fig. 2 Schematic diagram of the "Stop-Go Method" applied to simulation of the effect of the isotope exchange reaction between the growing UF_5 particles and UF_6 gas. The lateral axis represents time, and t_1 , t_2 , and t_3 denote collision times. White and black circles denote UF_6 molecules and UF_5 monomers, respectively.

tively, the relationship between S and P can be expressed as $S=2^P$. (2) The time scale of Process 1 is so very short that one can ignore the effect of the $f(a)$ term in Eq. (3). (3) The reaction volume is constant where the mass balance is satisfied. This approximation is called the "stop-go method" proposed by Wilhelm⁶⁾, and was applied to simulation of a continuous kraft digester reported by Takeuchi et al.⁷⁾.

The number of surface UF_5 molecules (M_s , M_6) depends on the UF_5 particle size. In this

Table 1 The relationship between the total number of atoms in a cluster and the ratio of surface atoms for each cluster size

Number of all atoms (2^P)	Ratio of surface atoms (τ)
2-8	1.00
13	0.92
38	0.84
55	0.76
147	0.63
201	0.61
561	0.45
1 249	0.39
2 406	0.31
4 033	0.27
6 226	0.24

work, UF_5 particles are assumed to grow in the form of a cubic octahedron as in the case of a rhodium (Rh) metal cluster. Table 1 summarizes the relationship between the number of all atoms (2^P) and the ratio of surface atoms (τ) in each cluster size⁸⁾ (since we assume UF_5 particle growth obeys Ulrich's model shown in Fig. 2, P is an integer greater than or equal to zero for UF_5). The plot of τ as a function of P is shown in Fig. 3.

The relationship between τ and

P can be expressed as the following equations for approximation:

$$\tau=1 \quad (0 \leq P \leq 3) \quad (5a)$$

$$=1-0.0844(P-3) \quad (3 \leq P \leq 13) \quad (5b)$$

$$=5.72/(2^P)^{1/3} \quad (13 \leq P) \quad (5c)$$

The Eq. (5c) in the case of P greater than

Fig. 3 The dependence of the ratio of surface atoms to total atoms of a cluster (τ) as a function of P (abscissa). The number of UF_5 molecules in a particle is 2^P .

13 was derived from an assumption that the UF_6 particle was perfectly spherical. From Eqs.(2)–(5), we could obtain the following kinetic equations taking the UF_6 particle growth into account.

$$dL_5/dt = k(L_8M_5 - L_5M_8) \quad (6)$$

$$dM_5/dt = -k(L_8M_5 - L_5M_8) \quad (7)$$

$$k = ((d_0 + d_p)/2)^2 \pi \omega (8RT/\pi \mu)^{1/2} \quad (8)$$

where, d_0 and m_0 represent the diameter ($=0.65$ nm) and the mass number ($=352$) of UF_6 molecules, respectively. R and T denote gas constant and absolute temperature.

And,

$$S = 2^P \quad (9)$$

$$d_p = \delta \cdot S^{1/3} \quad (10)$$

$$\mu = m_0 \cdot m_p / (m_0 + m_p) \quad (11)$$

$$m_p = 333 \cdot S \quad (12)$$

where, S , d_p , μ , and m_p denote the number of UF_6 molecules in a particle, the diameter of UF_6 particles, the reduced mass number of a UF_6 molecule and a UF_5 particle, and the mass number of UF_5 particles, respectively. The collision time, t_c , between UF_5 particles of S is also given by the following equation:

$$t_c = (\pi m_p / 8RT)^{1/2} / (2^{1/2} \pi r_p^2 N_p) \quad (13)$$

where r_p and N_p denote the radius and the number of UF_5 particles consisting of UF_5

molecules of S .

Then, we numerically solved Eqs.(5)–(13) using the Runge-Kutta-Gill computational method.

3. Results and Discussion

We applied this calculation method to estimate the influence of the isotope exchange reaction between the growing ^{235}U enriched UF_5 particles and natural UF_6 gas, using Eqs. (6)–(13). Figure 4 shows a typical result of the time dependence of isotopic ratios, $^{235}\text{U}/^{238}\text{U}$, in both gas and solid phases, while UF_5 particles grow up to a diameter of 10 nm starting from 4% ^{235}U -enriched UF_5 monomers of 1 μg and natural UF_6 of 1 mg. The reaction volume is here assumed to be 5 cm^3 . As shown in Fig. 4, it is found that the influence of Eq.(1) seems to be negligible in the particle growth region from one molecule to the diameter of 10 nm. Although the effect of the surface area of UF_5 particles is considered to be more serious in Process 1 compared to that in Process 2, this effect seems to be negligibly small in this calculation. This can be qualitatively explained in terms of the product of reaction time (t) and the τ . Since the exchange reaction probability used in these systems is the same value as the static system, the magnitude of the influence depends on τt . For Process 1, since $t=10^{-3}$ and $\tau=0.1$ –1 from Fig. 3, then the product, τt , is 10^{-4} to 10^{-3} . On the other hand, since $t=10^3$ and τ is at least greater than 10^{-2} for Process 2, then $\tau t > 1$. Consequently, the influence of Process 1 on the separation factor can be estimated to be less than 10^{-3} times smaller than that of Process 2. Our calculated result of Fig. 4 is therefore reasonable.

4. Concluding Remarks

We applied our proposed simple calculation method to estimate the influence of the isotope exchange reaction on RI-

Fig. 4 Time dependence of the isotopic ratios, $^{235}\text{U}/^{238}\text{U}$, in both gas and solid phases during UF_5 particle growth up to a diameter of 10 nm. This was simulated for the exchange reaction between 1 μg of 4% ^{235}U -enriched UF_5 monomers and 1 mg of natural UF_6 gas.

MLIS for the growing ^{235}U enriched UF_6 particles-natural UF_6 gas reaction system. By use of the exchange reaction probability of 1.1×10^{-9} , the influence was found to be negligible for this system. However, there are some reservations. First, the Grigore'v, kinetic model, especially the $f(a)$ term, has not yet been experimentally verified. Second, the exchange reaction probability (ω) of 1.1×10^{-9} based on his assumptions needs to be reexamined for well-defined experimental conditions. Finally, the value of ω may be a function of the surface conditions and the cluster size. Further systematic investigations of this gas-growing particles reaction are now under way in our laboratory.

References

- 1) Kuga, Y., Endoh, S., Satooka, S., Okada, Y., Tashiro, H. and Takeuchi, K.: *J. Nucl. Sci. Technol.*, **28**, 870-872 (1991)
- 2) Grigore'v, G.Yu., Dorofeev, S.B., Zamilov, V.A., Kolesnikov, O.N. and Terent'ev, A.A.: *Sov. J. Chem. Phys.*, **3**, 2275-2281 (1986)
- 3) Onoe, J., Kuga, Y., Isomura, S. and Takeuchi, K.: *J. Nucl. Sci. Technol.*, **28**, 777-779 (1991)
- 4) Ulrich, G.D.: *Combustion Sci. Technol.*, **4**, 47-57 (1971)
- 5) Ohtsuka, K., Yamamoto, H. and Yoshizawa, A.: *Nihon Kagaku Kaishi*, 869-874 (1984)
- 6) Wilhelm, R.H. and Sweed, N.H.: *Ind. Eng. Chem., Fundamentals*, **8**, (2), 221-226 (1969)
- 7) Takeuchi, K., Komiyama, H. and Suzuki, M.: *J. Tech. Assoc., Pulp and Paper Ind.*, **62**, 111-114 (1979)
- 8) Hidai, M. and Ichikawa, M.: "Introduction to Homogeneous and Heterogeneous Catalysts", pp. 96-97, Maruzen, Tokyo (1983)

要 旨

成長粒子・ガス反応系のシミュレーションのための新しい計算方法

尾上 順, 空閑良壽, 武内一夫

理化学研究所 351-01 埼玉県和光市広沢 2-1

成長粒子とガスとの反応は分子法レーザーウラン濃縮プロセスにおいて重要な系である。なぜなら、分離係数低下の原因と考えられる濃縮 UF_6 の粒子成長時における天然 UF_6 ガスとの間で同位体交換反応が上記反応系に当てはまるからである。この反応系が分離係数に与える影響を見積るために、われわれは新しい簡便な計算方法を開発した。交換反応確率として Grigore'v らが報告している値、 1.1×10^{-9} 、を採用する限り、上記交換反応の影響は無視できるほど小さいことという結果が得られた。