An Anomalous Isotope Effect of ^{235}U in U(IV)−U(VI) Chemical Exchange

Y. Fujii, M. Nomura, and M. Okamoto

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama Meguroku, Tokyo 152, Japan

H. Onitsuka, F. Kawakami, and K. Takeda

Uranium Enrichment Research Laboratory, Asahi Chemical Industry Co. Ltd., Takeshimacho, Hyuga, Miyazaki-ken 883, Japan

Dedicated to Professor J. Bigeleisen on the occasion of his 70th birthday

The abundance ratios of ^{234}U, ^{235}U, ^{236}U and ^{238}U were determined by mass spectrometry on uranium samples obtained from a chromatographic uranium enrichment process based on the U(IV)−U(VI) chemical exchange reaction. According to standard theory, the elementary isotope effect in processes based on equilibrium chemical exchange is proportional to the mass difference of the isotopes. In the present work this has been confirmed for ^{234}U, ^{236}U and ^{238}U. However, according to the observed data the fractionation between ^{234}U and ^{235}U is much smaller than the one between ^{235}U and ^{236}U in spite of the same mass difference in either isotopic pair. The anomaly of the fractionation is concluded to be due to the characteristics of ^{235}U, which is the only odd mass number isotope in the present system.

Introduction

Chemical exchange isotope separation is based on quantum effects in the molecular vibrations of isotopic compounds [1]. As a general rule, in the high temperature regime the elementary isotope effect (deviation of the equilibrium constant from unity) is expected to be proportional to the difference of the isotopic masses and inversely proportional to the square of the mean isotopic mass. This tendency has been confirmed by the experimental isotope effects of light and middle heavy elements in various chemical exchange systems and suggests that isotope effects are very small in uranium chemical exchange systems.

A relatively large value of 1.0013 in aqueous solution at room temperature has been reported for the equilibrium constant r_{12}^{IV}/r_{12}^{VI} ($r_{12} = [^{238}U]/[^{235}U]$) in the U(IV)−U(VI) exchange system [2−5]. The strong bonds between the oxygens and uranium in the U(VI) ion, $O=U=O^{2+}$, would suggest that ^{238}U is enriched in U(VI). However, experimentally the light isotope ^{235}U is enriched in $O=U=O^{2+}$ (and therefore the heavier ^{238}U is enriched in U^{4+}); this finding has not yet been explained. Detailed information on the vibrational frequencies of the uranium complexes would be vital to elucidate the isotope effects of the U(IV)−U(VI) exchange system.

In order to learn more about the isotope effects in the U(IV)−U(VI) chemical exchange system, in the present work the separation behavior between four different isotopes of uranium is studied. Among the uranium isotopes other than ^{235}U and ^{238}U, ^{234}U and ^{236}U are long-lived and thus suitable for our study. ^{234}U exists in natural uranium at the very low concentration of 0.0055 atom % [6], but it is enriched along with ^{235}U in the gaseous diffusion and gas centrifuge processes. In addition, ^{236}U is contained in reprocessed and also in enriched uranium, due to the accumulation of ^{236}U in existing uranium enrichment plants which deal with both natural and reprocessed uranium. Thus it was possible to observe, along with ^{235}U and ^{238}U, the enrichment behavior of ^{234}U and ^{236}U by using commerically available enriched uranium.

Experimental

An uranium isotope separation by anion exchange chromatography, similar to the previously reported ones [2−5], was performed using Ti^{3+} and Fe^{3+} ions
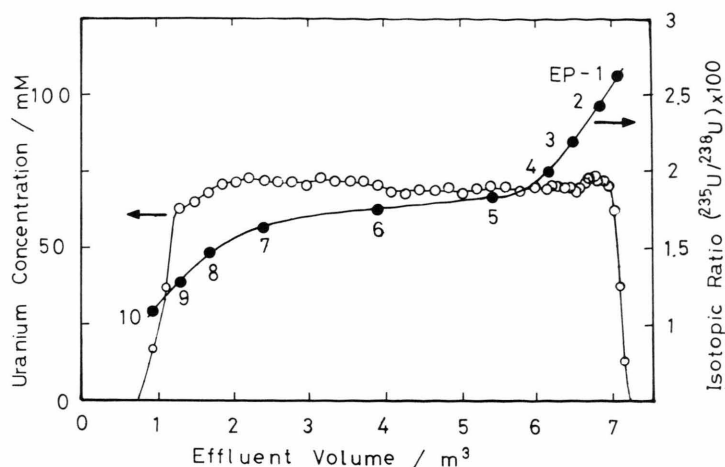
Fig. 1. Chromatographic profile of uranium concentration and $^{235}U/^{238}U$ ratio. Isotope analyses of ^{234}U, ^{235}U, ^{236}U and ^{238}U were made on the numbered samples.

as reductant and oxidant, respectively. The feed material was 1.76% ^{235}U enriched uranium. Two columns (3 m long and 1 m I.D.) are repeatedly used to obtain sufficiently high enrichment. After the chromatographic operation, the effluent was collected in fractions, the uranium concentration was determined by photospectrometry, and the uranium isotope analysis was done with a mass spectrometer MAT 261 equipped with a thermal ionization ion source. The abundances of ^{234}U, ^{235}U and ^{236}U were measured by using a secondary electron multiplier (SEM) detector, and the $^{235}U/^{238}U$ ratios were measured with a Faraday-cup detector. The calibration between the SEM and Faraday detectors was checked and shown to be satisfactory, as further explained in the next section.

Table 1. Isotopic abundance ratios in the sample fractions.

Fraction No.	$[^{234}U]/[^{235}U]$ $\times 10^3$ *	$[^{236}U]/[^{235}U]$ $\times 10^3$ *	$[^{235}U]/[^{238}U]$ $\times 10^2$
EP-1	8.386	1.891	2.6123
EP-2	8.265	1.949	2.4299
EP-3	8.172	2.050	2.2001
EP-4	8.041	2.119	2.0042
EP-5	7.959	2.210	1.8384
EP-6	7.884	2.242	1.7550
EP-7	7.835	2.316	1.6319
EP-8	7.703	2.447	1.4676
EP-9	7.526	2.601	1.2728
EP-10	7.381	2.744	1.0859
Original	7.913	2.221	1.7943

* The correction for the SEM detector has been made on the directly observed ratios by multiplying with a factor $(234/235)^{1/2}$ or $(236/235)^{1/2}$.

Results and Discussion

The chromatographic uranium band profile and the enrichment curve for ^{235}U are depicted in Fig. 1; isotope analyses of ^{234}U, ^{235}U, ^{236}U and ^{238}U were performed on the numbered samples, the values being given in Table 1. The Faraday-cup detector converts an ion beam into an electric current which gives the isotopic abundance by the recorded peak height. On the other hand, the electron emission by an ion beam at the first stage of the SEM depends on the ionic mass M; it is proportional to $(M)^{-1/2}$ [7]. Therefore, on using the SEM detector system the isotopic ratio is obtained by multiplying the recorded ratio of the peak heights with the square-root of the mass ratio of the isotopes, as mentioned in Table 1. To test the reliability of the present detector system, the isotopic ratio of

^{234}U and ^{238}U of uranium in Sample EP-1 was measured directly by a Faraday-cup detector. The observed value in the test is 2.194×10^{-4}, which is in good agreement with the value of 2.191×10^{-4} obtained as the product of two isotopic ratios, $^{234}U/^{235}U$ as measured with the SEM detector, and $^{235}U/^{238}U$ as measured by using the Faraday-cup (cf. Table 1). The uncorrected value is 2.196×10^{-4}.

The local enrichment factor for a pair of isotopes a and b in the j'th sample fraction is defined as

$$\alpha(a/b)_j = r(a/b)_j/r(a/b)_0 , \qquad (1)$$

where $r(a/b)$ is the abundance ratio, and the subscript 0 denotes the original material.

If a column, containing two isotopes (a and b), is in the stationary state, one has [8]

$$\alpha(a/b)_j = \exp[\varepsilon(a-b) z_j/H_{ab}] , \qquad (2)$$

where $\varepsilon(a-b)$ is the elementary isotope effect, z_j is the distance of the sample j from the sample 0, and where H_{ab}, the height of an equivalent theoretical plate, is proportional to the effective interdiffusion coefficient D_{ab} of a and b. If the mixture contains four isotopes, a, b, c, and d, three of them being rare, this column theory for binary mixtures is still applicable to the pairs ab, ac, etc., and one has from (2):

$$\ln \alpha(a/b)_j / \ln \alpha(a/c)_j = [\varepsilon(a-b)/\varepsilon(a-c)] (D_{ac}/D_{ab}) . \quad (3)$$

For our isotopes of mass 234, 235, 236 and 238 the ratios $\varepsilon(a-b)/\varepsilon(a-c)$ are expected to have values between $1/4$ and 4, while D_{ac}/D_{ab} may be of the order $\sqrt{(m_a+m_b)/(m_a+m_c)}$ or even closer to unity. On neglecting this factor and taking into account that (3) is also applicable when the stationary state is not yet reached, provided the α values are close to unity [8], we use the relation

$$\ln \alpha(a/b)_j / \ln \alpha(a/c)_j = \varepsilon(a-b)/\varepsilon(a-c) \quad (4)$$

for the discussion of our results.

The so called three-isotope plots, frequently used to analize isotope fractionations in geochemistry, are suitable for this discussion:

If $\ln \alpha(^{236}U/^{238}U)_j$ is plotted as a function of $\ln \alpha(^{234}U/^{238}U)_j$, the ten experimental points lie on a straight line with the slope $1/2$, as expected from (4), the r.h.s. of (4) having the value $1/2$ according to the general rule mentioned in the Introduction. If, however, experimental α_j-values involving ^{235}U are plotted, surprisingly the general rule is not obeyed. This is demonstrated in Figure 2. The experimental points lie again on straight lines, which shows the good quality of the measurements, but the slopes of these lines are anomalous. One finds

$$\varepsilon(^{234}U - {}^{235}U)/\varepsilon(^{235}U - {}^{238}U) = 0.14 \pm 0.02 \quad (5)$$

and

$$\varepsilon(^{236}U - {}^{235}U)/\varepsilon(^{235}U - {}^{238}U) = -0.43 \pm 0.03 \quad (6)$$

instead of 0.333 and -0.333, respectively. Linear regressions [15] based exclusively on the data in Table 1 yield 0.145 ± 0.004 and -0.432 ± 0.009, respectively.

In Fig. 3 the values of (5) and (6) are plotted vs. the mass number. If the usual mass dependence of isotope effects were obeyed by our four isotopes, the two experimental values in Fig. 3 would lie on the straight line connecting the reference points (235.0) and (238.1). ^{234}U and ^{236}U seem to obey the general rule with respect to ^{238}U since the experimental values lie on a
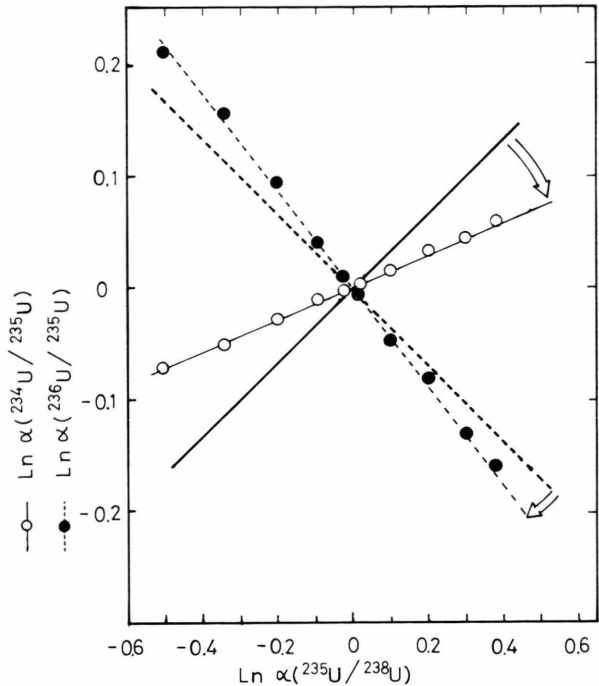

Fig. 2. Correlation of observed local enrichment factors of ^{234}U, ^{235}U, ^{236}U and ^{238}U. Theoretical relations are drawn by bold lines: the solid line for $^{234}U/^{235}U$ and the broken line for $^{236}U/^{235}U$.
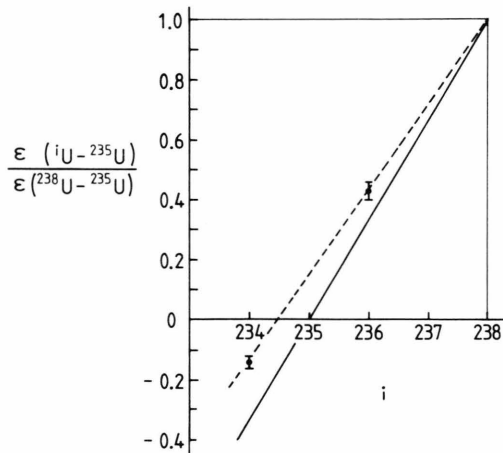

Fig. 3. Values of (5) and (6) vs. mass number.

straight line through the reference point (238.1), and ^{235}U seems to behave as if its mass number were 234.5.

Irregular isotope distributions have been observed in several cases, and it has been a controversial issue

in the field of geo- and cosmo-chemistry. Anomalous distributions of ^{16}O, ^{17}O and ^{18}O in meteorites have been reported by Clayton et al. They suggested that one has to do with mixtures from different isotopic sources whose isotopic abundance ratios are originally different [9]. Heidenreich III *et al.*, on the other hand, observed an isotopic anomaly in the formation of ozone from oxygen gas by discharge in laboratory experiments [10]. So far the experimentally observed anomalies of isotope effects are limited to special cases of non-thermal (energetic) kinetic processes, such as high temperature distillation of oxides (where the anomaly is observed as a second order effect of Rayleigh distillation) [11], and kinetic processes involving radicals in a magnetic fields [12]. An anomalous isotopic fractionation in equilibrium, such as described here, has not yet been reported. Our system involving both even and odd number isotopes, effects of nuclear

spin may contribute to the anomaly, as suggested by the theory of rotational molecular spectra [13, 14]. The contribution of the spin effect may become the more important, the smaller the value of $\Delta m/m^2$ of the isotopes involved, as is the case with uranium.

In conclusion, the present experiment demonstrates that the uranium isotope effect in the U(IV)–U(VI) chemical exchange system is proportional to the mass difference for the isotopes ^{234}U, ^{236}U, and ^{238}U, while ^{235}U behaves as if it would have the mass 234.5.

Acknowledgement

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