Chemical State of Uranium-239 in Neutron-Irradiated Uranium(IV) and Uranyl(VI) Sulfate Solutions

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Very few investigations have been devoted to study the chemical state of ^{239}U in neutron-irradiated uranium compounds. In 1939, Irvine[1] reported probable

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[1] J. Irvine, Jr., *Phys. Rev.*, **55**, 1105 (1939).

formation of quadrivalent ^{239}U in neutron-irradiated ammonium uranyl acetate solution and its enrichment with respect to ^{238}U in the first fraction of a hydrolytic precipitation by a factor of the order of ten. On the other hand, Aten, Beers and De Groot[2] reported that quadrivalent and sexivalent uranium isolated from U_3O_8 irradiated with slow neutrons have the same specific activity of ^{239}U. The following experiments have been carried out by the present authors to study the chemical state of ^{239}U in neutron-irradiated uranium-(IV) and uranyl(VI) sulfate solutions.

TABLE I

COMPOSITION OF THE SOLUTIONS (in moles)

	U(VI)	U(IV)	SO_4^{--}*	H^+
Soln. A**	0.02	—	1.9	2.8
Soln. B	0.02	0.02	1.9	2.8
Soln. C	—	0.02	1.9	2.8

* SO_4^{2-} was supplied as sulfuric acid and sodium sulfate.

** Nitrogen gas was passed through the Soln. A.

Three kinds of target solution were made up as shown in Table I, and 100 ml. of each solution in a glass vessel was exposed for one hour to a neutron flux of $\sim 10^7/\text{cm}^2/\text{sec}$. During irradiation, the container of the solution was covered with a black paper to keep the whole system in the dark. In addition, it was cooled with ice to reduce the velocity of isotopic exchange reaction between uranium(IV) and uranium(VI)[3]. After irradiation, either uranyl(VI)- or uranium(IV) sulfate was added to the solutions A and C, so that the solutions became 0.02 M in both uranyl-(VI)- and uranium(IV) sulfate. The separation of uranium(IV) from uranium(VI) was carried out with portions of the resulting solution within 30 minutes after the end of irradiation. The uranium(IV) fraction was extracted with chloroform as cupferronate. After the solvent and the excess of cupferron were removed from the chloroform layer, the residue was dissolved in nitric acid. To the resulting solution containing uranium(VI) were added ammonia water to precipitate ammonium diuranate. The precipitate was dissolved in a hot mixture of acetic and nitric acids; finally sodium uranyl acetate was precipitated from the solution. The uranium(VI) fraction in the aqueous layer after the chloroform extration was treated in a similar way as above to precipitate sodium uranyl acetate. All precipitates of sodium uranyl acetate were dried, mounted on a stainless-steel dish and submitted to counting with a thin end-window Geiger-Müller counter. The decay of the activity was followed for more than three half-lives of ^{239}U, and the distribution of ^{239}U in uranium(VI) and uranium(IV) fractions was calculated. The results are shown in Table II.

TABLE II

RADIOACTIVITY OF ^{239}U IN EACH FRACTION

	^{239}U in U(VI) fraction		^{239}U in U(IV) fraction	
	c.p.m.	%	c.p.m.	%
Soln. A	7200	97	250	3
Soln. B	9750	75	3280	25
Soln. C	4630	61	2930	39

Remarks: Decay correction was made for each fraction. If U(III) were formed, it should be air-oxidized to U(IV) state during the separation procedure and counted as U-(IV) fraction.

In another experiment with the solution C, it was found that ^{239}U is enriched in the uranium(VI) fraction by a factor of approximately 50. From those data, the following conclusions can be drawn.

i) Most part of ^{239}U in the neutron-irradiated uranyl(IV) sulfate solution is in the sexavalent state.

ii) More than half of ^{239}U in the neutron-irradiated uranium(IV) sulfate solution is not in the quadrivalent state, but in the sexavalent state.

iii) Hot-atom effect plays an important role in the formation of ^{239}U in the sexivalent state, since ^{239}U is enriched in the uranium(VI) fraction separated from the neutron-irradiated uranium(IV) sulfate solution.

The details of this work will be reported elsewhere.

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[2] A. Aten, Jr., M. Beers and D. De Groot, *J. Inorg. Nucl. Chem.*, **5**, 159 (1958).

[3] R. Betts, *Can. J. Research*, **26B**, 702 (1948).