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 COMMUNICATIONS TO THE EDITOR
 

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NEPTUNIUM(VI) IN MOLTEN NITRATES<sup>1</sup>

Sir:

There has been no direct evidence for the existence of neptunium(VI) in any molten salt system. In molten chlorides,<sup>2</sup> neptunium has been prepared in the (III), (IV) and (V) states. In molten nitrates,<sup>2</sup> the LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic, only Np(V) has been observed. A study of the solvent extraction<sup>3</sup> of neptunium from the LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic showed a large increase in the distribution coefficient upon the addition of NH<sub>4</sub>NO<sub>3</sub>. This fact could be explained by either a "salting effect" or by a valence change. This work has shown that Np(V) is oxidized to Np(VI) by the action of NH<sub>4</sub>NO<sub>3</sub> in the LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic.

The reaction vessel was fabricated from a 10-mm. quartz absorption cell which was fused to a 20-cm. length of 12 mm. quartz tubing. This cell fitted into a small furnace<sup>4</sup> which fitted into the cell compartment of a Cary Recording Spectrophotometer Model 14. The spectral measurements in the molten nitrates were carried out at 182°.

Neptunium-237 in dilute HNO<sub>3</sub> was placed in the reaction vessel and carefully dried by evacuating and heating. Filtered, molten LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic was added to the cell and the resulting green solution yielded the spectrum of Np(V). The addition of NH<sub>4</sub>NO<sub>3</sub> to the melt resulted in bubbling and spectral measurements showed the Np(V) peak at 9820 Å. to decrease and a new peak at 11,600 Å. to grow in. The next day the Np(V) peak had decreased to only 2% of its original value. The color of the melt changed from bright green to a brownish yellow.

Since the major peak of Np(VI) in perchlorate solution is at 12,230 Å.,<sup>5</sup> the spectrum of Np(VI) in concentrated nitric acid was measured. In this case the major peak occurred at a still shorter wave length, 11,220 Å.

The action of NH<sub>4</sub>NO<sub>3</sub> in molten nitrates is extremely interesting. For instance, NpO<sub>2</sub> is insoluble, in molten nitrates. However, the addition of NH<sub>4</sub>NO<sub>3</sub> to the melt at a temperature of 250° will dissolve the oxide quickly to yield Np(V) in solution. UO<sub>3</sub>, which is insoluble in molten nitrates, is dissolved easily by the action of NH<sub>4</sub>NO<sub>3</sub>. NH<sub>4</sub>NO<sub>3</sub> dissolves many metallic oxides in the molten nitrate system.<sup>6</sup> It acts as both an acid and an oxidizing agent in molten nitrates.

The Np(VI) ion is not stable in the nitrate melt and in a matter of days this ion will revert to the

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) D. M. Gruen, S. Fried, P. Graf and R. L. McBeth, "The Chemistry of Fused Salts," U. N. Peaceful Uses of Atomic Energy, Proceedings of the Second International Conference, Geneva, Sept., 1958, Vol. 28, paper P/940.

(3) N. M. Isaac, P. R. Fields and D. M. Gruen, paper given at 138th meeting ACS, New York, N. Y., "Solvent Extraction of Actinides and Lanthanides from Molten Salts."

(4) J. P. Young and J. C. White, *Anal. Chem.*, **31**, 1892 (1959).

(5) W. C. Waggener, *J. Phys. Chem.*, **62**, 382 (1958).

(6) This observation has also been reported by N. M. Isaac, P. R. Fields and D. M. Gruen, *J. Inorg. Nuclear Chem.*, in press.

(V) state. Also the Np(VI) ion is not stable with respect to higher temperatures. At about 220° the Np(VI) is reduced to Np(V). The Np(V) ion is stable in nitrate melts to about 350°. At 380° neptunium precipitates from the solution and as yet the brown solid has not been identified; however, it probably is NpO<sub>2</sub>.

The oxidation of Np(V) to Np(VI) also may be accomplished by bubbling ozone through the solution of Np(V) in the nitrate melt. Sometimes during this oxidation a brown precipitate forms. Work is now in progress to identify this solid.

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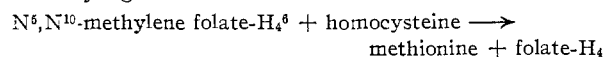
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 A METHYLATED DERIVATIVE OF  
TETRAHYDROFOLATE AS AN INTERMEDIATE OF  
METHIONINE BIOSYNTHESIS<sup>1</sup>

Sir:

In a recent communication<sup>4</sup> a report has been made of an enzymatic system isolated from a mutant<sup>5</sup> of *Escherichia coli* (113-3, Davis, grown on vitamin B<sub>12</sub> and methionine) which is capable of carrying out the reaction



This enzymatic system is comprised of several cofactors (DPNH, FAD, ATP, Mg<sup>++</sup>) and two enzymes, which have now been partially purified. One enzyme is the component missing in another

(1) This work was supported by a grant-in-aid from the National Science Foundation. Brief reports of the isolation of an intermediate of methionine biosynthesis have been made by this laboratory<sup>2</sup> and by Wilmanns, *et al.*<sup>3</sup>

(2) A. R. Larrabee and J. M. Buchanan, *Federation Proc.*, **20**, 9 (1961).

(3) W. Wilmanns, B. Rücker and L. Jaenicke, *Z. physiol. Chem.*, **322**, 283 (1960).

(4) F. T. Hatch, A. R. Larrabee, R. E. Cathou and J. M. Buchanan, *J. Biol. Chem.*, **236**, 1095 (1961).

(5) B. D. Davis and E. S. Mingioli, *J. Bacteriol.*, **60**, 17 (1950).

(6) Abbreviations used are: folate-H<sub>4</sub>, tetrahydrofolate; DPNH, diphosphopyridine nucleotide (reduced form); FAD, flavin adenine dinucleotide; ATP, adenosine triphosphate.

(7) F. Pregl and J. Grant, "Quantitative Organic Microanalysis," The Blakiston Company, Philadelphia, Pa.

(8) This observation was made by Dr. Victor Herbert.

(9) R<sub>f</sub> = 0.31 in 0.1 M phosphate buffer, pH 7.0.

(10) ADDENDUM.—Since this communication was submitted for publication a paper by Keresztesy and Donaldson has appeared which describes some recent studies on pteroyl A, a compound isolated by them from horse liver. In consultation with these authors at the Federation Meetings in April 1961 several properties of their compound resembled those of the intermediate of methionine biosynthesis, N<sup>5</sup>-methyl folate-H<sub>4</sub>, reported by us at that time. Keresztesy and Donaldson<sup>11</sup> have now synthesized this compound (as have Sakami and Ukstins<sup>12</sup>) by reduction of N<sup>5</sup>,N<sup>10</sup>-methylene folate-H<sub>4</sub> with borohydride and have shown that it may be converted to formaldehyde and folate-H<sub>4</sub> by their enzymatic system. We have now prepared this compound synthetically by their method and have found that it contains one mole of methyl group per mole of folate compound. It is converted in our enzymatic system to methionine but to only one-half the extent of the enzymatically prepared compound.

(11) J. C. Keresztesy and K. O. Donaldson, *Biochem. and Biophys. Res. Comm.*, **5**, 286, 289 (1961).

(12) W. Sakami and I. Ukstins, *J. Biol. Chem.*, **236**, PC50 (1961).