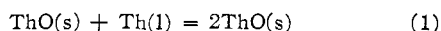

 COMMUNICATIONS TO THE EDITOR

VAPOR PRESSURE OF THORIA¹

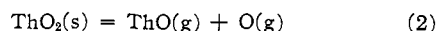
Sir:

The existing high temperature thermodynamic data for thoria are in marked disagreement, and some of the vaporization processes inferred to be important are subject to criticism. The most recent determination of the vapor pressure was carried out by Hoch and Johnston² by means of tantalum effusion cells. They obtained a heat of sublimation at 2150°K. of 154 kcal./mole, which does not agree with Shapiro's³ value of 170 kcal./mole.

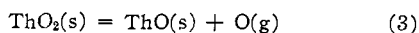
Hoch and Johnston² present three conclusions. First, the reaction



deduced from high temperature X-ray studies, proceeds to the right above 1850° and to the left below 1850°. Second, the reaction



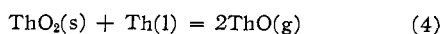
accounts for 2 to 10% of the volatility of ThO₂(s). Third, the reaction



occurs to an appreciable extent at 2500°K. Using their data one can show that these conclusions are mutually inconsistent.

If the first conclusion is correct, then ΔF_1° for reaction (1) is approximately zero at 1850° and since ΔF° of formation of ThO₂(s) is $-292,760 + 46.01 T$ cal./mole,^{3a} ΔF° of formation of ThO(s) is $-146,380 + 23.00T$. Estimating an entropy for reaction (1) one finds ΔF_3° 82,500 cal./mole at 2500°K., which yields an equilibrium pressure for reaction (3) of 9.6×10^{-10} atm. Since the ThO(g) pressure must be less than or equal to this value depending on whether ThO(s) is present, the maximum possible pressure of ThO(g) is 9.6×10^{-10} atm. Hence, the maximum mole per cent. of ThO(g) is about $8 \times 10^{-3}\%$ rather than 2-10%.

If the second conclusion is correct, then starting with $\Delta F_2^\circ = -2RT \ln (0.05p_{\text{ThO}_2})$ at 2500°K., one finds that the reaction



produces a ThO(g) pressure of 2×10^{-5} atm. at 1850°. A pressure this large would have caused complete evaporation of a 1/32" diameter X-ray sample in about 30 minutes.

The authors surmise that the first conclusion is the most reliable even in spite of the possible complication introduced by the melting of thorium at a temperature near the observed reaction temperature. Hence, it appears doubtful that reaction (2) *per se* is of importance at 2500°K.

The possibility exists that tantalum reduces ThO₂(s) at very high temperatures thereby in-

creasing its volatility. Recently, preliminary effusion measurements with ThO₂(s) using a tungsten cell yielded a vapor pressure of 1.05×10^{-4} atm. at 2828°K., which is about 0.2 times the value obtained by Hoch and Johnston. The authors believe that the entropy of sublimation of ThO₂(s) must be about the same as that of UO₂(s), *i.e.*, 33 e.u. at 2800°K.⁴ Hence, a more reliable vapor pressure equation appears to be

$$\log p(\text{atm}) = -3.16 \times 10^4/T + 7.20 \quad (5)$$

which gives a heat of sublimation of 144.5 kcal./mole.

(4) R. J. Ackermann, Argonne National Laboratory Report ANL-5482 (September, 1955).

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RECEIVED MARCH 13, 1956

 PARTICIPATION OF GLUTAMINE IN THE BIOSYNTHESIS OF HISTIDINE¹

Sir:

Recent evidence indicates that histidine synthesis by microorganisms is not a reversal of its degradation,^{2,3} which proceeds through urocanic acid and formamidinoglutamic acid. While the final stages of histidine formation, *e.g.*, the conversion of imidazole glycerol to the amino acid, have been studied⁴ and the origin of C₂ has been investigated,^{3,5} nothing is known of the origin of the nitrogen atoms of the imidazole ring. In a study of imidazole ring synthesis we have found that, in *Escherichia coli*, the amide nitrogen of glutamine is a more efficient precursor of nitrogen 1 than ammonia, glutamic acid, or asparagine.

L-Glutamine-amide-N¹⁵ (32.5 atom % excess) was obtained by an unequivocal route with a 90% utilization of the added isotopic ammonia by the reaction of the mixed anhydride⁶ of carbobenzyloxy- α -benzyl glutamate⁷ and ethyl chlorocarbonate with N¹⁵H₃ and subsequent hydrogenolysis of the intermediate. *E. coli* was grown for 6 hours on a minimal medium⁸ (containing 1487 mg. of ammonia-N per liter) supplemented by a vitamin mixture.

(1) This work was supported in part by a grant from the National Institute of Neurological Diseases and Blindness (Grant B-226) of the National Institutes of Health, Public Health Service and by a contract between the Office of Naval Research and the Psychiatric Institute. Taken in part from a doctoral dissertation to be submitted by Amos Neidle.

(2) B. A. Borek and H. Waelsch, *J. Biol. Chem.*, **205**, 459 (1953).

(3) L. Levy and M. J. Coon, *ibid.*, **208**, 691 (1954).

(4) B. N. Ames, H. K. Mitchell and M. B. Mitchell, *THIS JOURNAL*, **75**, 1015 (1953); B. N. Ames and H. K. Mitchell, *J. Biol. Chem.*, **212**, 689 (1955); E. Adams, *ibid.*, **217**, 325 (1955).

(5) C. Mitoma and E. E. Snell, *Proc. Nat. Acad. Sci.*, **41**, 891 (1955).

(6) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

(7) H. Sachs and E. Brand, *THIS JOURNAL*, **75**, 4610 (1953).

(8) C. H. Grey and E. L. Tatum, *Proc. Nat. Acad. Sci.*, **30**, 404 (1944).

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

(2) M. Hoch and H. L. Johnston, *THIS JOURNAL*, **76**, 4833 (1954).

(3) E. Shapiro, *ibid.*, **74**, 5233 (1952).

(3a) J. P. Coughlin, *Bur. Mines Bull.*, **542**, p. 51 (1954).