COMMUNICATIONS TO THE EDITOR

VAPOR PRESSURE OF THORIA[1]

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 Johnston[2] 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's[3] value of 170 kcal./mole.

Hoch and Johnston[2] present three conclusions. First, the reaction

$$\mathrm{ThO(s) + Th(l) = 2ThO(s)} \qquad (1)$$

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

$$\mathrm{ThO_2(s) = ThO(g) + O(g)} \qquad (2)$$

accounts for 2 to 10% of the volatility of $ThO_2(s)$. Third, the reaction

$$\mathrm{ThO_2(s) = ThO(s) + O(g)} \qquad (3)$$

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 $ThO_2(s)$ 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 8×10^{-3}% rather than 2–10%.

If the second conclusion is correct, then starting with $\Delta F_2^\circ = -2RT \ln (0.05 p_{\mathrm{ThO_2}})$ at 2500°K., one finds that the reaction

$$\mathrm{ThO_2(s) + Th(l) = 2ThO(g)} \qquad (4)$$

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 $ThO_2(s)$ at very high temperatures thereby increasing its volatility. Recently, preliminary effusion measurements with $ThO_2(s)$ 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 $ThO_2(s)$ must be about the same as that of $UO_2(s)$, *i.e.*, 33 e.u. at 2800°K.[4] Hence, a more reliable vapor pressure equation appears to be

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

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

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

R. J. ACKERMANN
R. J. THORN
P. W. GILLIES

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PARTICIPATION OF GLUTAMINE IN THE BIOSYNTHESIS OF HISTIDINE[1]

Sir:

Recent evidence indicates that histidine synthesis by microörganisms is not a reversal of its degradation,[2,3] which proceeds through urocanic acid and formamidinoglutaric acid. While the final stages of histidine formation, *e.g.*, the conversion of imidazole glycerol to the amino acid, have been studied[4] and the origin of C_2 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-N^{15} (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 anhydride[6] of carbobenzyloxy-α-benzyl glutamate[7] and ethyl chlorocarbonate with $N^{15}H_3$ and subsequent hydrogenolysis of the intermediate. *E. coli* was grown for 6 hours on a minimal medium[8] (containing 1487 mg. of ammonia-N per liter) supplemented by a vitamin mixture.

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