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

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

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

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

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

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

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 $\Delta F_2^\circ = -2RT \ln (0.05 p_{ThO_2})$ at 2500°K., one finds that the reaction

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

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

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

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

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

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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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TABLE I

DISTRIBUTION OF N^{15} IN HISTIDINE

Experiment No. →	1		2		3[a]	
	N^{15} atom % excess[b]	N derived from amide N, %	N^{15} atom % excess	N derived from amide N, %	N^{15} atom % excess	N derived from amide N, %
Histidine	2.10	6.5 (8.1)[c]	2.68	8.2 (10.3)	2.80	8.6 (10.7)
α-NH_2-N	.71	2.2 (2.8)	.89	2.7 (3.4)	1.00	3.1 (3.8)
N-3	.55	1.7 (2.1)	.82	2.5 (3.1)	.57	1.8 (2.2)
N-1 calcd.[d]	5.0	15 (19)	6.3	19 (24)	6.8	21 (26)
N-1 found	5.0	15 (19)				
Protein glutamic acid N	.73	2.2 (2.8)				

[a] Procedure was identical to experiments 1 and 2 except that asparagine replaced ammonia in the medium. [b] All samples were diluted four-fold with unlabeled N prior to analysis except for the glutamic acid isolated from the enzyme digest which was diluted 32-fold. [c] The values in the brackets are the per cent. amide N incorporated corrected for dilution by the original inoculum (approximately 20% of the final 500 mg. of protein). [d] Calculated by difference $3 \times 2.1 - 0.71 - 0.55$.

This culture (250 ml.) was used to inoculate one liter of the same medium, at which time 52 mg. of isotopic glutamine (5 mg. amide-N 32.5 atom % excess N^{15}) was added, an addition which was repeated after one hour. After a total of 3.5 hours of incubation at 37° with shaking, the cells were separated by centrifugation and the protein was obtained by treatment with cold and hot trichloroacetic acid, ethanol, ethanol–chloroform–ether mixture, and ether. Histidine was precipitated and recrystallized as the bis-3,4-dichlorobenzene sulfonate,[9] after prior isolation from the hydrolyzed protein as the mercury salt.[10] Stepwise degradation to urocanic acid and glutamic acid was effected by successive digestion with heat-treated and unheated extracts of *Pseudomonas fluorescens*.[11] By the first digestion ammonia corresponding to the α-amino group of histidine was obtained, the second digestion liberating nitrogen 3 of the imidazole ring as ammonia. Glutamic acid (N-1 of histidine) was recovered from the enzyme digests by the Foreman procedure[12] and recrystallized as the hydrochloride. Determinations of the N^{15} concentration in the different samples were carried out with a Process and Instruments mass spectrometer, which was kindly made available to us by Dr. S. Graff.

The high incorporation of glutamine amide nitrogen into N-1 in the presence of a 180-fold excess of ammonia (experiments 1 and 2) or a 90-fold excess of asparagine amide-N (experiment 3) points to the participation of glutamine or a compound derived from it in an early stage of histidine biosynthesis. Since our data (N^{15} incorporation into the α-amino group of histidine and protein glutamic acid) showed that glutamine is concentrated by the cells in preference to ammonia, the possibility might be visualized that N-1 is derived from intracellular ammonia originating in the amide group and not in equilibrium with the α-amino group of glutamic acid. The results obtained (experiment 3) with cells grown on asparagine as the major nitrogen source argue against this possibility.

The question arises whether the amide group of glutamine participates directly in histidine synthesis by primary formation of an amino sugar or an amino aldehyde or indirectly by group transfer from an intermediate such as guanine.

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RELATIVE RATE CONSTANTS FOR REACTION OF OH RADICAL WITH SULFURIC ACID, FORMIC ACID AND CEROUS ION

Sir:

Hydrogen does not readily react[1,2] with OH radical in 0.4*M* sulfuric acid. Allen[3] has suggested that this may be due to complexes, such as $H_2SO_5^-$ or HSO_4, formed by OH radical with sulfuric acid. The relative reactivity of OH radical with sulfuric acid has been quantitatively determined by a study of the gamma irradiation of 0.4*M* sulfuric acid solutions containing mixtures of ceric ion, cerous ion and formic acid.

The 100 e.v. yields of the initial products H, OH, H_2 and H_2O_2 in the radiolysis of water are denoted by G_H, G_{OH}, G_{H_2} and $G_{H_2O_2}$. The 100 e.v. yield of any product in the radiolysis of aqueous solutions is denoted by G(product). In the radiolysis of ceric ion–cerous ion–formic acid mixtures, $G(Ce^{++++})$ increases with decreasing $(Ce^{+++})/(HCOOH)$ ratio at any constant cerous ion concentration while at constant $(Ce^{+++})/(HCOOH)$ ratio $G(Ce^{++++})$ decreases with decreasing total concentration of cerous ion and formic acid. These data are quantitatively interpreted by the assumption that three solutes compete with each other for reaction with OH radical

$$Ce^{++} + OH \longrightarrow Ce^{+++} + OH^- \quad (1)$$

$$HCOOH + OH \longrightarrow HCOO + H_2O \quad (2)$$

$$H_2SO_4 + OH \longrightarrow HSO_4 + H_2O \quad (3)$$

Whether it is H_2SO_4, HSO_4^- or $SO_4^=$ which reacts with OH radical has not been determined but it will be assumed for kinetic treatment to be H_2SO_4 in

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