

amounts are subtracted from the total amount of each isomer found by infrared analysis; the differences are treated by the method of Ingold to give first approximations to the desired rate constant ratios. The process is repeated until sufficiently exact values have been obtained for these ratios. The final values are listed in Table II.

The data provide two independent tests of the accuracy of this treatment. One of these concerns the nearness to zero of the parenthetical values in cols. 6 and 7 of Table II. These isomers were absent initially, and thus owe their presence completely to the "parasitic" deuteroprotonation reaction. The mean of the parenthetical values is +0.012, and the mean deviation is ± 0.014 . In view of the analytical precision, ± 0.016 , these values do not appear to be significantly larger than zero. The other, less sensitive, check of the treatment has to do with the good consistency of the pseudo first-order rate constants for *para*-protodeutera-

tion listed in the last column of Table II. These constants were obtained from the "corrected" concentrations shown in column 8 of Table II. If the method of correction were inappropriate, such consistency would hardly be expected.

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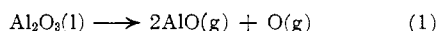
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COMMUNICATIONS TO THE EDITOR

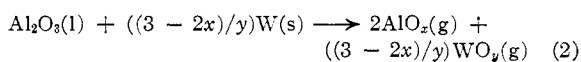
GASEOUS OXIDES OF ALUMINUM, TUNGSTEN, AND TANTALUM¹

Sir:

Brewer and Searcy² have concluded that $\text{Al}_2\text{O}_3(1)$ vaporizes from a tungsten effusion cell at 2300–2600°K. according to the equation



They deduced that a reaction of the type



does not occur by a comparison of the weight of effusate collected with a chemical analysis for aluminum contained therein. They inferred, since Al_2O_3 is more volatile in a tantalum than in a tungsten cell, that the former reduces Al_2O_3 to $\text{Al}_2\text{O}(g)$ whereas the latter does not. Confident that stable tungsten oxide molecules exist at these temperatures, the authors have investigated directly the weight ratio of Al_2O_3 to tungsten transported upon complete vaporization of the Al_2O_3 .

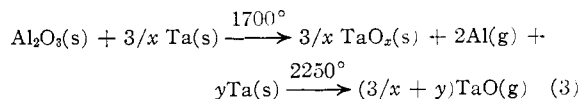
The outgassed tungsten cell was mounted in an evacuated water-cooled fused silica condenser. No radiation shields were employed except annular shields directly on the top of the cell to control the temperature of the top relative to that of the bottom. Hence only an insignificant amount of the effusate experienced reflection.

In a preliminary experiment it was found by spectroscopic analysis that tungsten had been transported to the condenser but not to a target at about 450°. The weight of material on the target agreed approximately with that found by Brewer and Searcy. Subsequent experiments yielded a weight ratio of Al_2O_3 to tungsten transported of 1.17 ± 0.02 at 2587°K. No deposition occurred below the orifice plane. It was also observed that

milligram quantities of tungsten were transported within the effusion cell from one region to another at a higher temperature. Since the vapor pressure of tungsten is negligible at these temperatures, one concludes that tungsten is transported out of the cell by a gaseous oxide which is sufficiently unstable to cause transportation of tungsten by dissociation within the effusion cell. Hence, some oxygen must effuse out of the cell and the experimental weight ratio of Al_2O_3 to tungsten must be greater than that which one calculates assuming $\text{WO}_y(g)$ to be undissociated. This fact definitely eliminates only the products $\text{AlO}(g) + \text{WO}_3(g)$. For the possible combinations, $\text{Al}_2\text{O}(g) + \text{WO}(g)$, $\text{AlO}(g) + \text{WO}(g)$, and $\text{Al}_2\text{O}(g) + \text{WO}_3(g)$ the weight ratios are 0.28, 0.55, and 0.83, respectively.

Langmuir³ has shown indirectly that $\text{WO}_3(g)$ exists at high temperatures. However, more detailed experiments are needed to distinguish among the other possibilities. In spite of this, the fact remains that Al_2O_3 and tungsten do react at high temperatures and that the free energies measured by vaporization of Al_2O_3 in a tungsten crucible correspond more closely to reaction (2) rather than (1).

The reaction with tantalum is more easily understood. The authors find that Al_2O_3 appears to vaporize from a tantalum cell according to the reaction



on the basis of the metallic aluminum deposited on the condenser and the weight ratio of Al_2O_3 to tantalum transported of 0.19.

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

(2) L. Brewer and A. W. Searcy, *THIS JOURNAL*, **73**, 3308 (1951).

(3) I. Langmuir, *ibid.*, **35**, 105 (1913).