cies ZH_2/ZO_2 and ZD_2/ZO_2 in the chain-breaking processes $X + O_2 + M$, where X is the chain-carrier and M is H_2, D_2 or O_2. Experimentally these values are 3.1 and 2.1, respectively; whence $ZH_2/ZD_2 = 1.5$. This value compares favorably with the value $ZH_2/ZD_2 = \sqrt{\mu D_2/\mu H_2} = \sqrt{4/2} = 1.4$, roughly calculated from the simple theory of three-body collision frequency [Grant and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 29 (1933)], assuming equal collision diameters for H_2 and D_2. For according to this, the ratio ZH_2/ZD_2 is a function only of the reduced masses, μ, of the respective complexes $(X + O_2 + H_2)$ and $(X + O_2 + D_2)$; and the reduced masses are approximately the masses of H_2 and D_2 when $X + O_2$ is large compared with H_2 and D_2. The whole of the observed change due to deuterium, therefore, can be accounted for on the basis of relative deactivating efficiencies. This leads to the observation that any additional changes, due to the substitution of deuterium for hydrogen, in the relative rates of chain branching and chain breaking process controlling the explosion limit, must cancel one another. It is unlikely that this would be the case if D and H or D_2 and H_2 were the chain carriers.

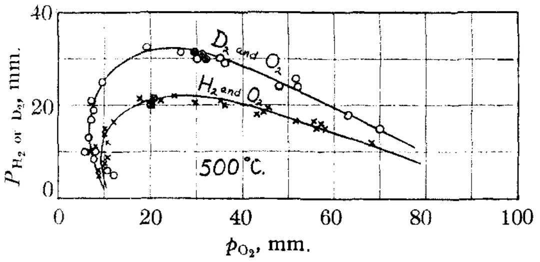

Fig. 1.—Explosion limits at 500°: X, hydrogen and oxygen; O, deuterium and oxygen; ☒, hydrogen diffused through palladium; ◉, deuterium diffused through palladium.

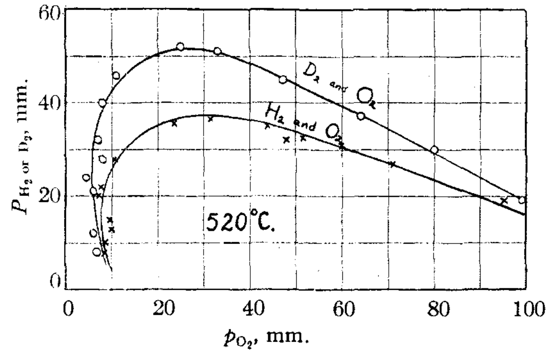

Fig. 2.—Explosion limits at 520°: X, hydrogen and oxygen; O, deuterium and oxygen.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
ARTHUR A. FROST
HUBERT N. ALYEA

RECEIVED APRIL 17, 1934

THE PREPARATION OF HYDROGEN COMPOUNDS OF SILICON

Sir:

In our studies on the kinetics of the catalytic decomposition of the hydrogen compounds of some of the fourth and fifth group elements it became necessary to prepare rather large quantities of silane, SiH_4. Being acquainted with the very favorable results obtained in the preparation of the germanes in liquid ammonia [Kraus and Carney, THIS JOURNAL, **56**, 765 (1934)], it was thought advisable to follow the same procedure in an attempt to prepare some of the silicon compounds, since the former were obtained in unusually high yields, three to four times as great as those found in the aqueous method [Dennis, Corey and Moore, *ibid.*, **46**, 657 (1924)].

Magnesium silicide, prepared by the direct combination of the elements, was dropped into a solution of ammonium bromide in liquid ammonia. A reaction was noticed to proceed immediately with the liberation of considerable quantities of gases, which upon examination were found to consist chiefly of hydrogen, silane and disilane, and of small amounts of trisilane. To date approximately 30 liters of these silanes have been prepared by this method, with yields ranging from 65 to 80% based on the silicon used in the preparation of the magnesium silicide. The yield obtained here is about three times as great as that found by Stock and co-workers [Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933, p. 21], who employed the analogous aqueous method.

THE GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
WARREN C. JOHNSON
T. R. HOGNESS

RECEIVED APRIL 18, 1934