*Gas Chromatography as a New Tool for Analyses of Hydrogen Isotopes**

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A mixture of hydrogen isotopes could completely be separated[1,2] by use of a technique of the gas adsorption chromatography, when the adsorption column was filled with "molecular sieves 5A"** and cooled in a liquid-nitrogen bath. Preliminary experiments were then carried out with special interest in applying the gas chromatography as a new tool for quantitative analyses of these hydrogen molecular species. In the followings a record of these will be presented.

Ordinary hydrogen and pure deuterium*** (>99.5%) were mixed in a ratio of 1.0 : 2.0 and reserved in a glass flask (sample I). A portion of this mixture was brought into contact with platinum-wire catalyst kept at 300°C overnight to reach isotopic exchange equilibrium (sample II). Chromatograms were obtained alternatively on the sample I and II by varying the sample volume. As the amount of deuterium is known in the sample I, the relation between deuterium amounts and peak heights or any other peak feature can be determined. Thus, it was found that a linear relationship, passing through the origin, holds between deuterium amounts and peak heights. The amount of deuterium in the sample II can now be estimated from the observed peak height by use of the calibration line just determined.

The amount of D_2 for a given volume of the sample II was found always smaller, as expected, than that before equilibration. Assuming that this difference in the deuterium content is due to the formation of HD and therefore corresponds to one-half of the amount of HD formed during the equilibration reaction, the amount of HD in the sample II was evaluated. Such a datum for HD is given in the Table I together with that of D_2 calculated according to the calibration line. The amount of H_2 in the sample II must now be equal to the total volume of the sample minus the sum of D_2 and HD.

In view of the rapid chemisorption and desorption of hydrogen on platinum catalyst at 300°C,[3] the hydrogen molecular species D_2, HD and H_2 in the sample II may well be expected to be in complete exchange equilibrium. In the last column of the table is shown the equilibrium constant K of the reaction as estimated from the data illustrated there.

Very slight inaccuracies in the deuterium amount of the sample II do affect the values for HD, H_2 and hence, K in the method of analysis used here. Thus, an error of about ±5% is anticipated for the value of K. The discrepancy between the observed K, 3.79, and the calculated one, 3.69[4] at a temperature of 300°C should therefore be convincing or the agreement is satisfactory.

It is concluded that the gas chromatographic techniques are convenient and powerful to analyze the amount of hydrogen molecular species D_2, HD and H_2 for both qualitative and quantitative purposes. The mass spectrometric method so far used for such purposes may be replaced to a certain extent by the gas chromatographic method.

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Table I

Amounts of hydrogen molecular species D_2, HD and H_2 before (I) and after (II) equilibration on platinum at 300°C.

Run	Isotope sample	Total volume of sample, ml. 20°C	Vol. of components, ml. 20°C			Equilibrium constant
			D_2	HD	H_2	$K=[HD]^2/[H_2][D_2]$
1	I	1.51	1.01	0.0	0.50	
2	II	1.21	0.540	0.532	0.138	3.79
3	I	0.947	0.632	0.0	0.315	

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1) S. Ohkoshi, Y. Fujita and T. Kwan, *Catalyst*, **15**, 1 (1958).

2) S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, **31**, 770 (1958).

** Linde Air Products Co., New Jersey, U. S. A.

*** Stuart Oxygen Co., San Francisco, U. S. A.

3) T. Kwan, *J. Res. Inst. Catalysis, Hokkaido University*, **2**, 81 (1949); *Advances in Catalysis*, **6**, 67 (1954) (Academic Press. New York).

4) H. C. Urey, *J. Chem. Soc.*, **1947**, 562.