Gas Chromatographic Separation of Hydrogen Isotopes D_2 and HD

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A simple gas adsorption chromatographic apparatus was constructed by us[1] with materials readily available in this physicochemical laboratory. The apparatus had the advantage of operating the adsorption column at any desired temperature and so far was used as a tool for analyses of

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

low boiling gases, however with potential purpose of separating and analyzing hydrogen isotopes D_2, HD and H_2. The latter investigation was now performed and led to a certain satisfactory aspect which will be described below.

Experience[1] has shown that the efficiency of gas chromatographic separation largely depends on the nature of column packings and on the temperature of the column. Experiments were therefore conducted primarily to find out most favorable column packing and temperature. As a result Pyrex glass U-tube of 80 cm. long and 0.3 cm. internal diameter was employed as a column and filled with "molecular sieve 5 A" due to Linde Air Co. New Jersey, the column being immersed, when working, in a liquid nitrogen bath.

Two hydrogen isotope samples were investigated for the purpose; one was pure deuterium (>99.5%) supplied by Stuart Oxygen Co. San Francisco and the other was prepared by contacting a mixture of pure deuterium and ordinary hydrogen in a ratio of 1.8 : 1.0 with a reduced nickel powder kept at 100°C to reach isotopic exchange equilibrium. Ordinary hydrogen from cylinder was used as a carrier gas, its flow rate being 70 ml. per min. A known amount of the sample gas under reduced pressure was introduced in a manner as described previously[1] into the stream of the carrier from the sample tube of known volume which was connected to sample reservoirs, mercury manometer and then to vacuum line. The thermal conductivity cell with thermistor was used to detect hydrogen isotopes. Now, under such experimental circumstances there appeared two distinct elution peaks, when a mixture sample after equilibration was introduced, which were almost perfectly separated with each other. In Fig. 1 is shown such a chromatogram which was recorded however by a commercial set of the gas chromatography-Shimazu GC-1A, No. 58035* recently furnished in this laboratory.

As shown in Fig. 1, it is apparent that the retention time for pure deuterium is coincident with that of the second peak

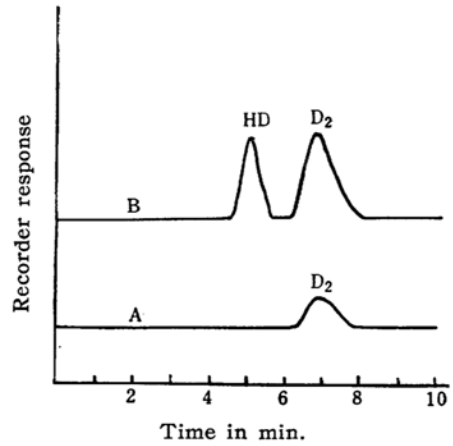

Fig. 1. Chromatogram of hydrogen isotopes. A: Pure deuterium. B: A mixture of D_2, HD and H_2 after equilibration at 100°C.

of the chromatogram for the mixture sample. Since ordinary hydrogen was employed as the carrier gas, H_2 in the mixture should not appear in the chromatogram. The first peak, therefore, should be identified as HD. It is interesting to note that coiled Pyrex column of the same length tended to have a slightly lower efficiency to separate hydrogen isotopes.

Attempts were made by Glueckauf and Kitt[2] to obtain pure deuterium from a mixture of D_2 and H_2 by using a column filled with palladium black-asbestos and kept between 0 and 100°C. Similar investigation was carried out by Tamaru[3] who used palladium-on-Celite as column packing. So far as we are aware, there is no report concerning complete separation of D_2 and HD by means of the gas chromatographic technique. The present finding surely proves the gas chromatography to be a new tool for quantitative as well as qualitative analysis of hydrogen isotopes; it is possible to proceed to determination of the amount of constituents D_2, HD and H_2 for a given volume of the mixture, if appropriate calibration data are beforehand arranged. Experiments are continuing along this line and will soon be published.

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* The function of this instrument is essencially the same with that constructed in our laboratory except that the thermal conductivity cell is equipped with coiled tungsten heater wires. The advantage of the commercial set may be the equipping of a self-recording system which we lack in ours. Its disadvantage, on the other hand, is a certain limitation in operating the column temperature, viz., it is designed primarily for above-room-temperature. The only modification was that the original stainless steel column arranged horizontally had to be replaced by a vertical glass U-tube.

2) E. Glueckauf and G. P. Kitt, "Vapor Phase Chromatography", Butterworths Scientific Publications, London (1957) p. 422

3) K. Tamaru, Private communication.