Enrichment of Deuterium by Low Temperature Gas Adsorption Chromatography

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(Received August 15, 1958)

In 1934 Taylor et al.[1] found that the separation of hydrogen isotopes H_2, HD and D_2 is effective by the use of the desorption of these molecules from the surface of active charcoal kept at liquid air temperature. Accordingly, the composition of the hydrogen sample desorbed during the last stage showed an increase in the amount of HD and D_2 compared with that of the initial gas. In recent years, Barrer[2] and others have shown that dehydrated zeolite gives rise to efficient adsorption characteristics in many respects. The finding has led to an idea of "molecular sieve" which was now made available by Linde Air Products Co. New Jersey in commercial scale. We employed the molecular sieve as column packing of the gas adsorption chromatography and were able to separate HD and D_2 at a column temperature of liquid nitrogen[3]. Further investigtions by us[4] proved that the gas chromatographic technique is useful for the analyses of H_2, HD and D_2.

In view of the remarkable efficiency with which HD and D_2 are separated chromatographically through a column, filled with molecular sieve 5A and immersed in a liquid nitrogen bath, attempts were made to enrich deuterium by passage of a mixture of hydrogen isotopes such a column. The result, though of preliminary nature as yet, seemed to be noteworthy and will be communicated here.

The apparatus[5] used for the investigation of hydrogenation kinetics was used without any particular modification for the present purpose. A glass flask of ca. 1 liter volume containing 330 mmHg hydrogen isotope mixture was connected to a U-shaped glass column filled with molecular sieve 5A, to a Töpler pump and then to a sample vessel of ca. 10 cc. volume. The column was of 30 cm. in length and 0.6 cm. in internal diameter. Mercury manometers were equipped between the sample flask and the adsorption column as well as between the column and the Töpler pump to read the pressure of hydrogen sample before and after passage through the column.

The experimental procedure was as follows: the apparatus was first evacuated at room temperature and then the column was immersed into a liquid nitrogen bath. A mixture of hydrogen isotopes was introduced, by opening the cock of the flask, into the column. Rapid adsorption of hydrogen on the packing took place with residual pressure of about 30 mmHg. The rate of passage of hydrogen through the column was however not so fast; it took more than 5 minutes to reach a few mmHg in a space between the column and the Töpler pump. The hydrogen once passed through the column was continuously collected by means of the Töpler pump, and a small portion of the collected hydrogen was analysed for the isotopic composition by the gas chromatographic technique developed by us[3].

It was found that the hydrogen sample collected initially contained neither HD nor D_2. The amount of HD, however, increased gradually with increase of the volume of the hydrogen passed, and finally D_2 was found to appear in the sample gas when the liquid nitrogen bath was removed from the column and adsorbed hydrogen sample was collected back into the original flask. The pressure of the hydrogen sample in the flask was 140 mmHg showing that about 60% of the hydrogen sample was passed through the column.

In Table I is shown the composition of hydrogen isotopes H_2, HD and D_2 before and after the passage.

Table I

Enrichment of deuterium by the low temperature gas adsorption chromatography

	Total vol. ml. 20°C	H_2		HD		D_2	
		ml.	%	ml.	%	ml.	%
Isotope sample before passage	435	196	45	100	23	139	32
Isotope sample after passage	184	20	11	32	17	132	72
Isotope sample* passed through	251	176	70	68	27	7	3

* Calculated from the volume of hydrogen sample before and after the passage.

The separation factor f of the hydrogen isotopes H_2 and D_2 is defined as

$$f = \frac{n'_{D2}}{n'_{H2}} \Big/ \frac{n_{D2}}{n_{H2}}$$

where (n_{H2}, n_{D2}) and (n'_{H2}, n'_{D2}) are the concentrations of H_2 and D_2 before and

1) A. J. Gould, W. Breakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).
2) R. M. Barrer, ibid., **47**, 82 (1950).
3) S. Ohkoshi, Y. Fujita and T. Kwan, This Bultin, **31**, 770 (1958).
4) S. Ohkoshi, S. Tenma, Y. Fujita and T. Kwan, ibid., **31**, 772 (1958).
5) S. Tenma and T. Kwan, *Catalyst*, **15**, 11 (1958).

after the passage respectively. From the data in the table the separation factor was found to be 92.

It is concluded that the low temperature gas adsorption chromatography is extremely efficient and very simple to enrich deuterium from a mixture of H_2, HD and D_2. Experiments are to be conducted to enrich deuterium from hydrogen isotope mixture of various concentrations including ordinary hydrogen.

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