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The Sensitive Gas Chromatography of Para-, Orthohydrogen, Hydrogen Deuteride and Deuterium[1)]

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A sensitive gas chromatograph of the reduced-pressure type was devised to analyze hydrogen nuclear spin isomers and isotopes, and its characteristics were studied in order to obtain the optimum conditions for analysis. It was shown that the para and ortho composition of 0.01 ml. S. T. P. of normal hydrogen could be determined within an accuracy of 1% by employing an alumina column cooled at −196°C, while the composition of 0.02 ml. S. T. P. of the equilibrated mixture of hydrogen, hydrogen deuteride and deuterium at 25°C could be determined within the same accuracy by employing an alumina column coated with manganese chloride. The alumina column was no longer capable of separating the spin isomers when it was treated above 350°C. Kinetic studies of the hydrogen-deuterium equilibration (21°C) and of the orthohydrogen conversion (−196°C), using the alumina as a catalyst, revealed that this strong activation creates active sites for the equilibration and the magnetic conversion which makes the peak separation obscure. The nature of these active centers was briefly discussed.

Since the nuclear spin isomers of hydrogen, para- and orthohydrogen, and isotopic molecules, including deuterium and tritium, were found, the method of measuring the thermal conductivity, originally developed by Farkas, has long been used for the analysis of their mixture, while mass spectrometry has been used for the analysis of the isotopes. These methods of analysis, however, are somewhat unsatisfactory, apart from their lack of convenience, the applicability of the thermal conductivity method is practically limited to the binary mixtures, while the mass spectroscopy can not be used for the analysis of the spin isomers.

Recently Kwan et al. and a number of other investigators have reported that it is possible to separate these isomers or isotopic molecules by gas chromatography when a column packing such as alumina is operated at a low temperature of liquid nitrogen.[2-11)] Moreover, the simultaneous separation of these four modifications, para-, orthohydrogen, hydrogen deuteride and deuterium molecules, has been successful.[12,13)] This method, therefore, may be a useful alternative to the current ones for the analysis if the present ambiguity in accuracy and the low sensitivity are improved, all the results reported hitherto, except for those in Venugopalan and Kutschke's work,[11)] indicate that it is necessary, for the quantitative determination of the composition, to use a gaseous sample of more than one milliliter at a standard temperature and pressure. In order to follow the change in composition at low pressure, it is desirable to develop a highly-sensitive apparatus which can work with a sample of several hundredths of a milliliter. For this purpose, a gas chromatograph of the reduced-pressure type was adopted, and the optimum conditions for the analysis were examined using the equilibrium mixture of hydrogen modifications.

The present paper will present the details of this method and also some information about the catalytic activities of gamma-alumina in the ortho-parahydrogen conversion and in the hydrogen-deuterium equilibration reactions which were studied by its application.

Experimental

Apparatus and Procedure.—A gas chromatograph of the reduced-pressure type was used in this study; a schematic diagram of it is shown in Fig. 1. The helium employed as the carrier gas was adjusted to atmospheric pressure by a bubbler (A) and was then purified over a Linde molecular sieve 13X trap (C) at −196°C. Gas sampling was performed by a gas pipette (D). In most experiments, an alumina column

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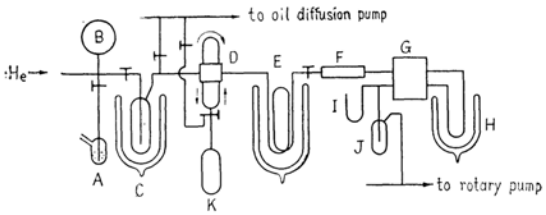

Fig. 1. Schematic diagram of the gas chromatograph.

A bubbler	G katharometer
B buffer	H U-tube trap
C moleculer sieve trap	I manometer
D gas sampling system	J pressure drop
E column	K reaction vessel or gas reservoir
F combustion furnace	

was used for the separation of isomers, and an alumina column coated with manganese chloride, for that of isotopes at −196°C. A Linde molecular sieve 13X column was also examined in order to compare it with the characteristics of these column packings. The eluted hydrogen samples were converted into water vapor on a cupric oxide column (F) heated at 750°C and were detected by a katharometer (G) made of stainless steel block with paths for the gas flow (5 mm. in diameter) and coiled tungsten filaments (30 ohms) in it. In order to avoid the condensation of water vapor, the katharometer was kept at 45°C, and the path between the combustion column and the katharometer, at 110°C. In order to maximize the sensitivity, the pressure in the katharometer was adjusted by a pressure drop (J) to 55—60 mmHg, which is the lowest value where the drifts of base lines are negligible.

Kinetic studies of the orthohydrogen conversion at −196°C and the hydrogen-deuterium equilibration at 21°C were made using column packings as catalysts. A reaction vessel of about 950 ml. with a circulator was connected with the gas pipette (D). The gases were left in contact with the catalyst for a suitable time and then led to the gas chromatograph for analysis. Prior to each experiment, the catalyst was degassed for 5 hr. at a definite temperature in vacuo better than 10^{-6} mmHg.

Materials.—Hydrogen was purified by diffusing it through a heated palladium thimble, while high purity deuterium purchased from the Takachiho Chemical Co. which contained hydrogen deuteride 0.7%, was used without further purification. Tank helium was passed through a trap filled with a Linde molecular sieve 13X immersed in liquid nitrogen in order to remove oxygen and other condensables; it was then used as the carrier gas.

Preparation of Columns.—Aluminum hydroxide prepared by the hydrolysis of distilled aluminum isopropoxide was dried at 500°C for 10 hr. in a current of dried air and was then left in contact with water vapor overnight. The alumina (80—100 mesh) thus obtained was packed into a glass tube (1.7 m. long and 2 mm. in inside diameter) and was treated in a current of helium under various conditions. The spectroscopic analysis of the alumina indicated that it contained iron 0.019%, manganese 0.002% and chromium 0.005% by weight. An X-ray diffraction study showed that this alumina had gamma structure.

The column for the separation of isotopes was prepared in the following way. Five grams of the alumina were immersed in 100 ml. of a 0.075 mol./l. manganese chloride solution overnight. The alumina was quickly washed with distilled water, dried at 200°C for 10 hr., packed into a glass tube (2.2 m. × 2 mm.), and then treated in a current of helium at 200°C for 25 hr. A Linde molecular sieve 13X (30—60 mesh) was also used as a column; it was packed into a glass tube (1.7 m. × 3 mm.) and treated in a current of helium at 100°C for 20 hr. The spectroscipic analysis of the molecular sieve indicated that it contained iron 0.12%, manganese 0.005% and chromium 0.005% by weight.

Results and Discussion

The Determination of Para- and Orthohydrogen.—As is shown in Fig. 2, chromatograms with two well-separated peaks were obtained by using an alumina column which was activated at 100—150°C. It was observed that the shape of the peaks at the beginning of activation was appreciably asymmetrical, but after activation for more than 20 hr. it became almost symmetrical. This treatment made it possible to evaluate the peak area by a rather simple method—by multiplying the height by the half-width of the peak. A column which was strongly activated at higher temperatures (350°C) no longer had the function

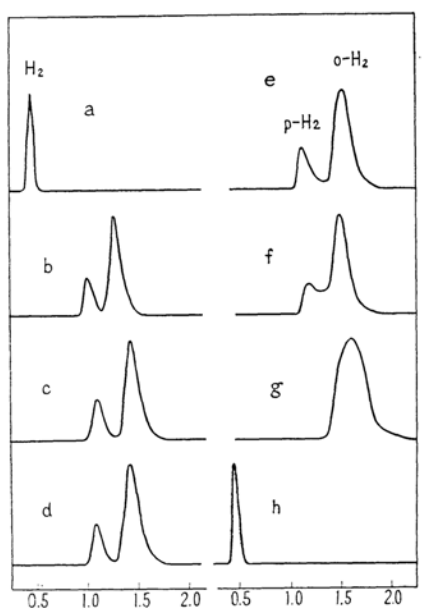

Fig. 2. Chromatograms of normal hydrogen on an alumina column activated at various temperatures.
Column: alumina (80—100 mesh, 1.7 m. × 2 mm.; −196°C) activated at a, 20°C, b, 100°C, c, 120°C; d, 150°C; e, 200°C, f, 270°C; g, 350°C; for 9 hr. and h, kept in contact with water vapor after activating at 350°C. Flow rate of carrier: 100 ml./min.

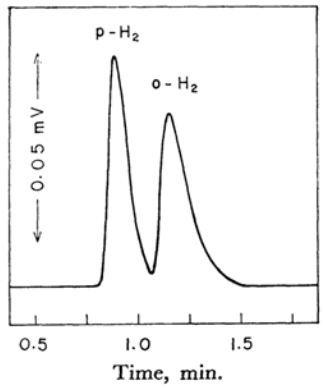

Fig. 3. Chromatogram of para-riched hydrogen equilibrated at −196°C.
Column: alumina (80—100 mesh, 1.7 m × 2 mm; −196°C) activated at 100°C for 45 hr.
Flow rate of carrier: 100 ml./min.
Sample: 0.015 ml.

of separation. However, it was easily recovered by the adsorption of water vapor. Figure 3 shows a chromatogram of the para-riched hydrogen obtained by the use of an alumina column. From a comparison of peak areas, it was established that the first-eluted peak corresponds to parahydrogen and the second peak, to orthohydrogen.

Figure 4 shows the calibration lines for these isomers. There was a good linear relationship between the peak area and the volume for each isomer; this relationship held up to 0.2 ml. of the sample. It was also shown that, for the analysis of normal hydrogen (para: ortho=1 : 3), it is sufficient to use more than 0.01 ml. of the sample,

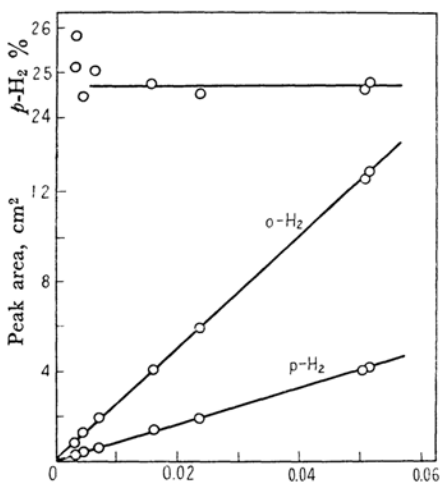

Fig. 4. Calibration lines for para- and orthohydrogen.
Column: alumina (80—100 mesh, 1.7 m. × 2 mm.; −196°C) activated at 100°C for 45 hr.
Flow rate of carrier: 100 ml./min.

and that the estimated mole fraction of the isomers agreed with the expected value within an accuracy of 1%.

The Linde molecular sieve 13X column has some unsatisfactory points. It gives not only longer retention times, but also a lower sensitivity than alumina. Moreover, the observed ratio of ortho to para in normal hydrogen becomes 2.88±0.03, which is lower than the expected value, 3.00. This is, as will be seen later, a result of the fact that the interconversion catalyzed by some paramagnetic impurities, mainly iron (0.12%), proceeds within the column. Therefore, it is advisable to employ highly-purified alumina as the column packing for the quantitative separation of para- and orthohydrogen.

The Determination of Hydrogen, Hydrogen Deuteride and Deuterium.—Analogous to the case of para- and orthohydrogen, well-separated chromatograms for isotopes were also obtained by using an alumina column coated with manganese chloride; they are shown in Fig. 5. The specific peak area which is defined as that for a unit volume of the sample, had the same value for both hydrogen and deuterium within the range of experimental error. Therefore, the ratio of the peak area for hydrogen isotopes corresponded practically to their mole ratios.

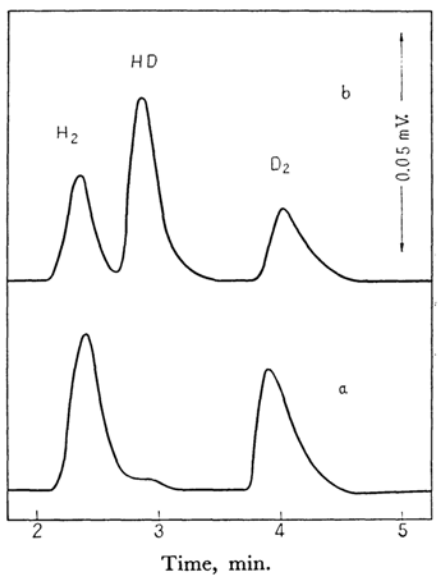

Fig. 5. Chromatograms of mixture of hydrogen, hydrogen deuteride and deuterium.
Column: alumina coated with manganese chloride and activated at 200°C for 25 hr. (80—100 mesh, 2.2 m. × 2 mm.; −196°C)
Flow rate of carrier: 90 ml./min.
a, mixture of hydrogen and deuterium (0.02 ml.) ($H_2/D_2=1.076$)
b, equilibrated mixture of hydrogen, hydrogen deuteride and deuterium at 25°C (0.022 ml.)

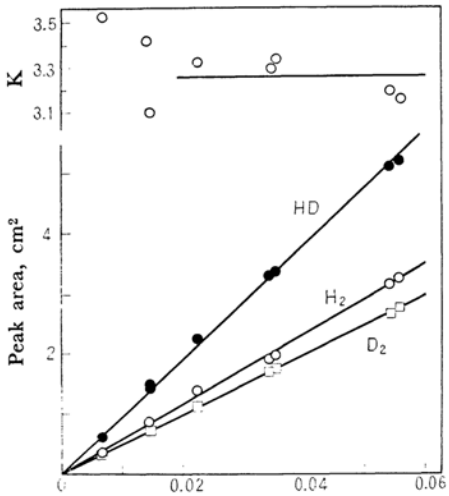

Fig. 6. Calibration lines for mixture of hydrogen, hydrogen deuteride and deuterium equilibrated at 25°C.
Column: alumina coated with manganese chloride and activated at 200°C for 25 hr.
(80—100 mesh, 2.2 m. × 2 mm.; −196°C)
Flow rate of carrier: 90 ml./min.

Figure 6 includes the calibration lines for these isotopes, which also held a good linear relationship between the peak area and the volume for each species. In this case of an isotopic mixture, it was verified, using an equilibrated mixture of hydrogen, hydrogen deuteride and deuterium at 25°C as the sample, that 0.02 ml. of a gaseous sample is sufficient for the quantitative determination of the composition within an accuracy of 1%. The observed value of the equilibrium constant, 3.26± 0.1, agreed with the calculated value, 3.268, within an accuracy of 3%. This improvement in sensitivity is mainly due to the lowering of the pressure of the carrier gas at which the katharomeer and to the conversion of eluted hydrogen into water, which amplifies the difference in thermal conductivity between the sample and the carrier gas.

Since a microthermal conductivity method can analyze 0.01—0.03 ml. of a sample,[14] the present method may be a useful alternative.

Orthohydrogen Conversion and Hydrogen-Deuterium Equilibration on Column Packings.—As is shown in Fig. 2, the separating power of alumina varied greatly according to the temperature at which alumina was activated. It has been reported that on separation occurs on a strongly-activated column; this is due to rapid interconversion between the isomers within the column.[7] In order to get further proof of this, kinetic studies of orthohydrogen conversion and also of hydrogen-deuterium equilibration were performed, using column packings as the catalysts.

The time course in all cases of constant pressure followed the first-order law; therefore, the rate constant may be expressed as:

$$k_e = (1/t) \ln (C_0/C_t) \text{ min}^{-1}$$

where C_0 or C_t is the excess concentration of species at time zero, or t, over the equilibrium value at the experimental temperature. The absolute rate constant was calculated to be:

$$k_m = k_e pV/60AkT \text{ molecules} \cdot \text{cm}^{-2} \text{ sec}^{-1}$$

where p is the gas pressure; V, the reaction volume at the temperature, T; A, the surface area of the catalyst, and k, Bolzmann's constant.

Figure 7 shows the specific activities for the conversion (−196°C) and for the equilibration (21°C) of catalysts which were subjected to the evacuation at various temperatures. Not all catalysts showed activity for the equilibration at −196°C. Therefore, the conversion proceeding at that temperature is of a physical nature.

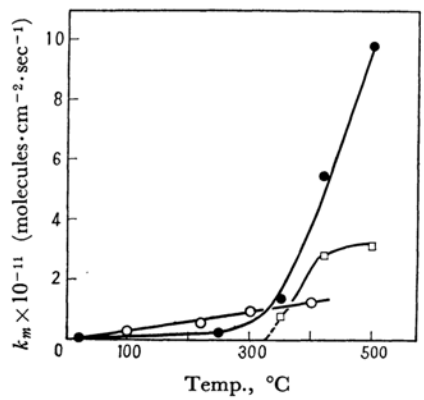

Fig. 7. Effect of evacuating temperature on the specific activities of catalysts.
● conversion on alumina at −196°C
○ conversion on molecular sieve 13X at −196°C
□ equilibration on alumina at 21°C

When the alumina was evacuated at temperatures higher than 350°C, the conversion activity increased abruptly; the equilibration activity also became appreciable at 21°C. On the contrary, the conversion activity of the molecular sieve 13X gradually increased with the evacuating temperatures, and the equilibration did not occur at temperatures up to 100°C.

As may be seen in Fig. 7, the activity of the physical conversion increases in two stages with the evacuating temperatures. The transition point between these stages nearly corresponds to the temperature at which the separated peaks begin to merge with each other, as is shown in Fig. 2. It may, therefore, be suggested that this phenomenon

14) H. Melville and B. G. Gowenlock, "Experimental Methods in Gas Reaction," Macmillan and Co., London (1964), p. 239.

results from the rapid interconversion within the column.

In order to get insight into this phenomenon, the effect of paramagnetic impurities was roughly examined by applying Wigner's theory. The activity of neodymium oxide in the parahydrogen conversion[15] was taken as a reference, and it was assumed that the conversion proceeds over the ferric ions on the surface of alumina the concentration of which is the same as that in bulk, and that the accessible distances between hydrogen molecules and active centers for γ-alumina and neodymium oxide are similar. The concentration of ferric ions is, therefore, given by the expression:

$$[Fe_2O_3]/[Nd_2O_3] = \{\mu(Nd^{3+})/\mu(Fe^{3+})\}^2 k_m(Fe^{3+})/k_m(Nd^{3+})$$

where $\mu(Fe^{3+})$ and $\mu(Nd^{3+})$ represent the magnetic monents of the cations. Thus the value of the concentration was estimated to be 0.04% by the evacuation at 250°C and 1.7% by that at 500°C. The former value agrees approximately with the observed iron content (0.019%), while the latter can not be explained from only its existence, even if all the ferric ions are exposed on the surface. Moreover, highly-purified alumina (Fe, Cu, Mg, and Mn$<$1 p. p. m.) which had been carefully prepared by three distillations of aluminum isopropoxide showed no activity in the evacuation at 250°C, but a high activity at 500°C, corresponding to a ferric ion content of 9.5%. Therefore, the first, gradual increase in activity is due to the exposure of paramagnetic impurities caused by dehydration, while the second, aburpt increase implies that "paramagnetic" sites of a different origin are created on the surface of γ-alumina.

Eley et al. have reported that α-alumina evacuated at 550°C has active sites for the H_2–D_2 equilibration and for the magnetic conversion, and also that new thermolabile paramagnetic sites are created by γ-ray irradiation.[16] Therefore, it is conceivable that α- and γ-alumina behave similarly in the catalysis of these reactions.

Further studies of the nature of these sites on γ-alumina are in progress; details will be reported later.

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16) G. J. K. Acres, D. D. Eley and J. M. Trillo, *J. Catalysis*, **4**, 12 (1965).