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Gas-Chromatographic Separation of Ortho- and Parahydrogen on Molecular Sieves:

Analysis, Preparation, and Measurement of Catalytic Conversion and of Adsorption

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Ortho- and parahydrogen has been separated on molecular sieves. An apparatus for the preparation of pure orthohydrogen and parahydrogen and for the determination of the conversion velocity in the presence of a catalyst is described. If the stationary phase acts as a catalyst during the separation an approximate determination of the conversion velocity can be made from the chromatogram. As there is a simple relationship between the retention volume and the first differential coefficient of the adsorption isotherm, the latter may be obtained from the peak corresponding to one of the components. The adsorption isotherms on molecular sieves Linde 13X and 5A are given. The adsorption enthalpies and the difference of the free enthalpies have also been calculated.

The successful preparation of pure parahydrogen by Bonhoeffer and Harteck (1) was made possible because they used a very simple method of analysis for the two spin modifications, viz., the measurement of the thermal conductivity of the gas.

After the existence of parahydrogen had been shown theoretically and also proved experimentally by the behavior of the specific heat of normal hydrogen, efforts were made to obtain at least one separate component. The result of thermodynamic calculations is that the equilibrium concentration of orthohydrogen may never exceed 75%, whereas practically pure parahydrogen can be obtained at very low temperatures. At 20°K the equilibrium concentration is 99.7% parahydrogen.

The first investigators were, therefore, trying to reach the low-temperature equilibrium, which is achieved very slowly in the gas phase. Giauque and Johnson (2) kept hydrogen liquid for some time and found a small change in vapor pressure which they attributed to the ortho–para conversion. Indeed, if hydrogen is kept in the liquid state for severals days, practically pure parahydrogen is obtained. The change of the vapor pressure is, however, very small, and, since the vapor pressures of the two components were not known at that time, only a small conversion in the direction ortho → para was assumed to have occurred in these experiments. Eucken and Hiller (3) measured the specific heat for analysis and tried to achieve equilibrium by using high pressures, with platinum as a catalyst. They obtained a measurable conversion. Finally the elegant method of Bonhoeffer and Harteck (1) to determine the ratio of ortho to para by measuring the thermal conductivity, which is proportional to the specific heat, led—together with the lucky choice of charcoal as a catalyst—to pure parahydrogen.

Experiments to obtain pure orthohydrogen were carried out at a much later date. As already mentioned pure orthohydrogen is not stable at any temperature, but, by using common methods of separation, it is possible to obtain orthohydrogen in a concentration > 75%, even up to

100%, as the mutual conversion of the two components is a very slow reaction. Also distillation may be an adequate method for enrichment, as there is a marked difference in the vapor pressures (orthohydrogen 751 mm Hg, parahydrogen 787 mm Hg at 20.4°K). However if we wish to obtain pure orthohydrogen the reaction

orthohydrogen → parahydrogen

in the liquid phase (4, 4a) is opposed to the effect of separation. This reaction is of second order with a velocity constant of 11×10^{-5} [% hr]$^{-1}$ (4b) corresponding to a conversion rate of 1%/hr at 100% orthohydrogen. It would, therefore, be possible to obtain a concentration of orthohydrogen of more than 99%.

For small quantities, the methods based on adsorption are *a priori* more adequate. However, at low temperatures a conversion which forms parahydrogen may take place in the adsorption layer. To prevent this, the adsorbent should not be paramagnetic. The unlike adsorption of para and orthohydrogen was first deducted from kinetic measurements, carried out with solid oxygen as a catalyst (4c). These measurements led to the conclusion that the difference in the free enthalpy of adsorption on oxygen was more than 80 cal. Early efforts of separation had been made on silica at 20°K (5): when the adsorption equilibrium was established, the main fraction had been pumped off. In the last fraction an enrichment of orthohydrogen was found. Recently Cunningham *et al.* (6) obtained practically pure orthohydrogen by fractional adsorption.

Gas chromatography which had in the meantime been developed, allows the quantitative separation of substances in one working process, even if the heats of adsorption differ very little. A separation with noncatalytic materials such as silica, zinc oxide, and aluminum oxide was to be expected.

In 1957, we began experiments for separating ortho- and parahydrogen (7, 7a). These experiments were suspended as shortly afterwards Moore and Ward (8) reported complete separation of the two components.* The experiments in our institute were taken up again in 1960 by Bachmann.

The necessity to cool the column with liquid nitrogen led to the use of short columns. With a 30-cm column, packed with zinc oxide, no separation could be obtained, whereas with the same length columns, packed with molecular sieves, the separation was excellent.

1. Experimental Method

Apparatus—The chromatograms were obtained partly with a self-constructed chromatographic apparatus of a common type and partly with a Perkin-Elmer fractometer 116 E.

Carrier gas—Helium, cleaned over Linde molecular sieves at the temperature of liquid air. Gas velocity—0.5–2 ml/sec.

Sample introduction—By gas sampling valve or syringe.

Column—Glass tubing 3–4 mm i.d., 10–30 cm long, filled with 0.5–5 g Linde molecular sieve dried in the carrier gas at 210°C. Grain size, 0.4–0.7 mm.

Thermostat—Dewar vessel with liquid oxygen, liquid nitrogen, liquid air (sometimes also under reduced pressure).

Detector—Thermal conductivity cell. Because in mixtures of helium and hydrogen the thermal conductivity is not always linear to the hydrogen concentration, results that are easier to evaluate can be obtained by oxidizing the hydrogen on its way from the column to the detector into water with CuO (see Moore and Ward (8). The sensitivity of the detection is then markedly higher and equal for ortho- and parahydrogen. To get reproducible results, the tubing between the CuO (heated to 250°C) and the detector must be heated up to at least 100°C. Otherwise the water coming through first is adsorbed on the walls of the tube and the first peak will be too small.

* For other references concerning gas chromatography of the hydrogen modifications and isotopes, see H. W. Habgood, *Ann. Revs. Phys. Chem.* **13**, in press.

2. Analysis

Figure 1 shows the complete separation of the two components of hydrogen. The chromatogram was obtained on iron-free molecular sieve 13X.†

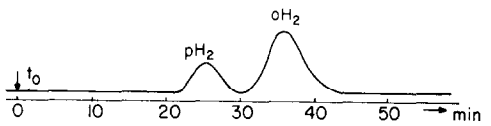

Fig. 1. Gas-chromatographic separation of ortho- and parahydrogen. Column—300 × 3.5 mm glass tubing filled with 3.5 g of iron-free Linde molecular sieve 13X activated at 210°C for 4 hr in a helium flow, 1 cc/sec; temperature—liquid oxygen; carrier gas—helium, 1 cc/sec; sample—1 ml H_2.

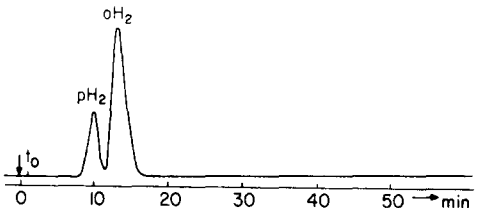

Fig. 2. Gas-chromatographic separation of ortho- and parahydrogen. Column first dried for 4 hr at 210°C in a stream of CO_2, then swept with helium at 20°C for 3 min. Temp., 90°K.

Figure 2 shows a chromatogram obtained with the same column as in Fig. 1, the only difference being that a previous heating had taken place in a stream of CO_2. Retention volumes and time of analysis decrease and the peaks become more symmetrical (8a). By heating the column in dry air, the amount of CO_2 retained on the column is much smaller and the decrease of the retention volume compared with columns heated in helium is correspondingly smaller.

The heating time for obtaining reproducible qualities of the column is, of course, dependent on the temperature. We always heated the columns uniformly at 210°C for 4 hr in the carrier gas.

When using a normal Linde molecular sieve 13X we could not obtain a complete separation. A small conversion takes place because of the iron content. With molecular sieve 5A we got a higher retention volume, but smaller ΔG-values (see Section 5b).

For the analysis of ortho- and parahydrogen the molecular sieve 13X is, therefore, more adequate. A complete separation is not necessary for a quantitative analysis and thus the time of analysis may be considerably shortened (9). For instance, analysis of 0.2-cc H_2 at 90% separation with 0.5-g molecular sieve 13X at the temperature of liquid air required only 5 min. The analytical error was 1%. The conversion on a normal, iron-containing molecular sieve is negligible (see Section 4), because analysis is possible in so short a time.

3. Preparation of the Pure Spin Modifications

To obtain the pure components, the mixture is separated with column A, as described in the preceding section and the ortho or para peak is adsorbed on a second column B, which is also packed with molecular sieve 13X and cooled with liquid air (see Fig. 3).

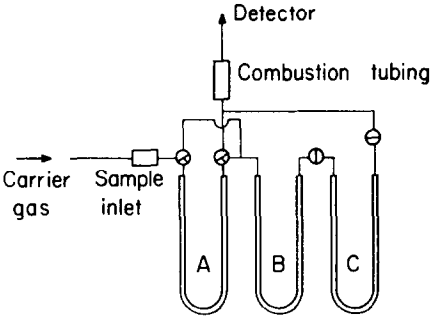

Fig. 3. Apparatus used for the preparation of pure ortho- and parahydrogen and for the determination of the conversion velocity $o\text{-}H_2 \leftrightharpoons p\text{-}H_2$ in presence of a catalyst in column B.

The purity of the component can be tested in a third column C. Helium is much less adsorbed than hydrogen and can, therefore, be separated from the component by pumping it off from column B at the temperature of liquid air. After a pump-

† We thank Dr. Hargitay, European Research Associates, Brussels, for giving us the material.

ing time of 1 min, 60% of the hydrogen was still on the adsorbent. No helium was found in this hydrogen, as proved by a second gas-chromatographic apparatus. If one pumps off for only 40 sec, more than 80% hydrogen is left adsorbed with a content of helium smaller than 0.5%. Thus in a very simple way one can obtain the pure modifications of hydrogen free from carrier gas.

4. Measuring the Catalytic Conversion on the Adsorbent

The apparatus for preparation of pure ortho- and parahydrogen described in the preceding section is also convenient for testing catalysts with the aid of the reaction

orthohydrogen → parahydrogen

or

parahydrogen → orthohydrogen

The pure ortho- or parahydrogen, respectively, is conducted in column B, the latter containing the catalyst to be tested. After a certain time the amount of conversion is determined in column C.

We have used this assembly to test the rate of conversion on iron-containing molecular sieves. Our aim was an approximate estimate of the effect of conversion on separation. For this purpose column B was filled with molecular sieves 13X, and parahydrogen was adsorbed and left on the column for a few minutes up to several hours. The data could be fitted to first-order kinetics. The half-life of the conversion on both the molecular sieves was between 4 and 6 hr, depending on the preliminary treatment. By previous treatment with CO_2 and by using iron-free molecular sieves, considerably smaller rates of conversion were found. Also the pollution of the column with oxygen (e.g., at the introduction of the sample or by a leak in the apparatus) causes a great increase of the conversion rate which may lead to a complete lack of separation (8a).

It is also possible to determine the velocity of conversion from the chromatograms obtained on columns that convert during the separation. Figure 4 shows a chromatogram on which an approximate evaluation is easily obtained. The peaks are in this case so far apart that no overlapping occurs from insufficient separation. Nevertheless, owing to a conversion during separation, the concentration between the two peaks does not decrease to zero.

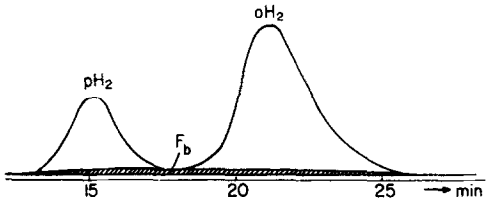

Fig. 4. Chromatogram obtained on a column catalyzing the $o\text{-}H_2 \rightleftharpoons p\text{-}H_2$ interconversion (molecular sieve 13X, containing iron).

We made the following simplifications:

1. We assumed that the rate of conversion of both components is equal, an assumption which is allowed as the ratio of ortho to para in equilibrium at the temperature of liquid air is approximately 1.

2. We took as retention time for both components the mid-point of the ortho and para values. The area corresponding to the amount converted is, then,

$$F_t = F_0 e^{-kt} \tag{1}$$

and

$$F_t = F_0 - F_b \tag{2}$$

where F_b is the area corresponding to the amount of hydrogen converted while passing through the column, and F_0 is the total area corresponding to the hydrogen introduced. If the peaks are very far apart, F_b is practically equal to the area under the "bridge" between the two peaks. In the case demonstrated in Fig. 4, F_b had been approximated as shown in the drawing.‡ From F_0 and F_b, we obtain F_t according to Eq. (2), and by putting this value in Eq. (1) a rate constant of the conversion $k = 9 \times 10^{-6}$ sec^{-1} can be calculated.

‡ Keller and Giddings (10) had already calculated the concentration profiles for mutual conversion of the components to be separated.

5. Adsorption Measurements

a. Correction of the Peak Broadening by Diffusion

It is possible to get the adsorption isotherms from a chromatogram (11). There is a simple relationship between the retention volume V_g (belonging to different concentrations between 0 and c_{max}) and the first differential coefficient of the adsorption isotherm:

$$V_{g(corr)} = F'(c) \qquad (3)$$

i.e., the retention volume $V_{g(corr)}$ (reduced to 1 g adsorbent and corrected for a diffusion coefficient $D_{eff} = 0$) is equal to the differential coefficient of the isotherm. There exist differential equations (12–14) for the calculation of the retention volumes. These equations take into account the influence of diffusion, but in the case of curved isotherms they cannot be integrated without special assumptions. With the aid of a computer the effect of diffusion on the retention volume may be calculated from the experimental data in each case.

It is also possible to choose the experimental conditions so that the first differential coefficient of the adsorption isotherm can easily be calculated from the differential equation. If the column is charged in such a way that the concentration profile is very flat on the diffuse side of the peak, the rate of broadening by diffusion on this side is very small and, by using short columns, nearly constant. Using two detectors (one at the beginning and one at the end of the column), one obtains two concentration profiles $c(t)$ which can be converted into $c(x)$ and thus make it possible to evaluate the differential equation.

To avoid this lengthy procedure of correction we will now describe some approximate corrections which apply to many cases.

1. The simplest assumption is that the rate of broadening by diffusion is equal on both sides of the peak. Hereafter the corrected curve lies halfway between front and rear sides of the peak. This correction is only an upper limit for the broadening on the rear side as, in the case of curved isotherms, the rate of diffusion is greater on the front than on the rear side.

2. Another possibility is to subtract the distance between the maximum retention time and the front side from the rear side; by this manipulation one obtains values lying between correction 1 and the measured rear side. It is easy to see that this correction gives the exact values for the two limits—symmetrical peaks (e.g., linear isotherms) and assymetrical peaks with vertical front side (e.g., steep curve of the isotherm and negligible diffusion).

The assumption that the rate of the maximum of the peak is not influenced by diffusion and that equilibrium is established on the front side as well as on the rear side is made for both corrections.

In the cases shown here the peaks are fairly symmetrical, i.e., the isotherms nearly linear. The difference between values, obtained after corrections 1 and 2, is very small. The front and the rear side also differ very little as to their shape and slope, and the difference of the values corrected *ad maximum* from the measured values is very small compared with the value of the whole retention. By making correction 2, we got better approximation to the true value (estimated error $<5\%$).

From the corrected curve one easily obtains the adsorption isotherm by an integration corresponding to Eq. (3).

b. Characteristic Quantities of Adsorption

If one supposes a certain analytical expression for $f(c)$, the validity of the presumed equation can be already seen from $f'(c)$. The numerical integration is, then, avoided as the constants are already obtained from the relationship $f'(c) = V_g$.

In our case the isotherms respond to the Ostwald-Freundlich relationship,

$$a = k \cdot p^n \qquad (4)$$

from which we obtain by differentiation

$$da/dp = knp^{n-1} = V_{g(corr)}/RT$$

and by taking logarithms,

$$\log (V_{g(corr)}/RT) = \log (k \cdot n) + (n - 1) \log p$$

Plotting log $(V_{g(\text{corr})}/RT)$ against log p produces straight lines. We easily obtain $(n\text{-}1)$ from the slope, and the value k from the intercept on the ordinate.

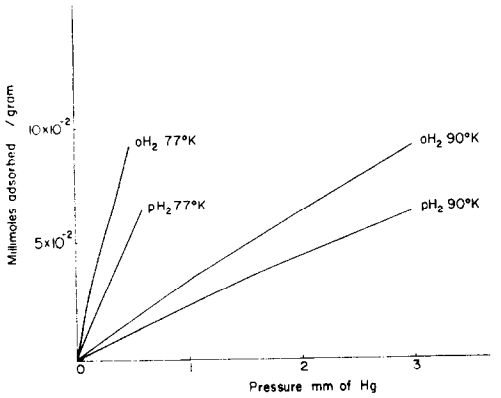

FIG. 5a. Adsorption isotherms of ortho- and parahydrogen on molecular sieve 13X.

Figures 5–7 show the chromatographically determined isotherms of ortho- and parahydrogen obtained on molecular sieves at different temperatures and after different previous treatment. Helium is very weakly adsorbed at these temperatures, as we found by separate static measurements, so that its presence does not influence the n-values of the isotherms.

The differential adsorption energies of the same charge can be calculated from the isotherms according to the equation

$$H = R\frac{T_1T_2}{T_1 - T_2}\,2.3(\log p_1 - \log p_2) \quad (5)$$

By taking logarithms, Eq. (4) gives

$$\log p = (\log a - \log k)/n \quad (6)$$

By substituting k and n from the isotherms (Fig. 5b) in Eqs. (5) and (6), the adsorption enthalpies are obtained,

$$H_{o\text{-}H_2} = -90.2 \log a + 1819 \text{ cal}$$

$$H_{p\text{-}H_2} = -90.2 \log a + 1611 \text{ cal}$$

respectively; by substituting $a = 1.5 \times 10^{-3}$ mmole/g,

$$H_{o\text{-}H_2} = 2.07 \text{ kcal/mole}$$

$$H_{p\text{-}H_2} = 1.87 \text{ kcal/mole}$$

and by substituting $a = 6 \times 10^{-2}$ mmole/g,

$$H_{o\text{-}H_2} = 1.93 \text{ kcal/mole}$$

$$H_{p\text{-}H_2} = 1.72 \text{ kcal/mole}$$

In earlier papers (15) one of the authors proposed and established the value ΔG which is in this case

$$\Delta G = RT \ln \frac{V_{g(\text{ortho})}}{V_{g(\text{para})}} = RT \ln \frac{t_{R(\text{ortho})}}{t_{R(\text{para})}}$$

as a characteristic quantity for the position of two substances in the chromatogram.

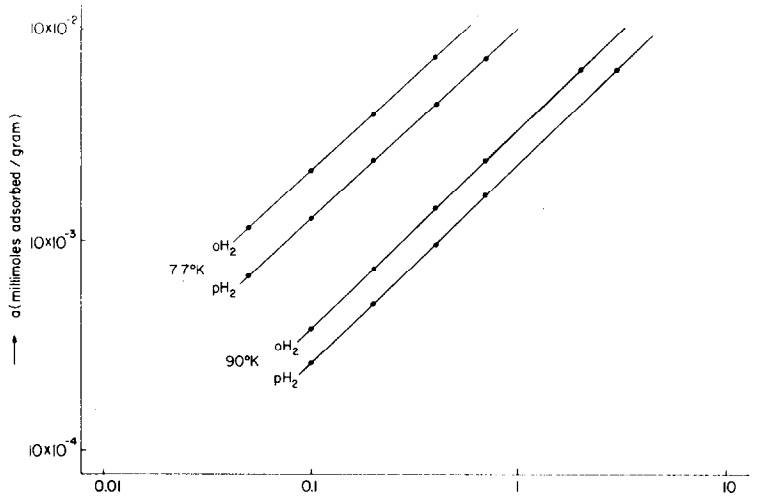

FIG. 5b. Logarithmic plot of values in Fig. 5a. At 77°K: $n = 0.91$; $k_{\text{para}} = 1 \times 10^{-1}$; $k_{\text{ortho}} = 1.7 \times 10^{-1}$. At 90°K: $n = 0.94$; $k_{\text{para}} = 2.3 \times 10^{-2}$; $k_{\text{ortho}} = 2.3 \times 10^{-2}$. (Abscissa, pressure in mm Hg.)

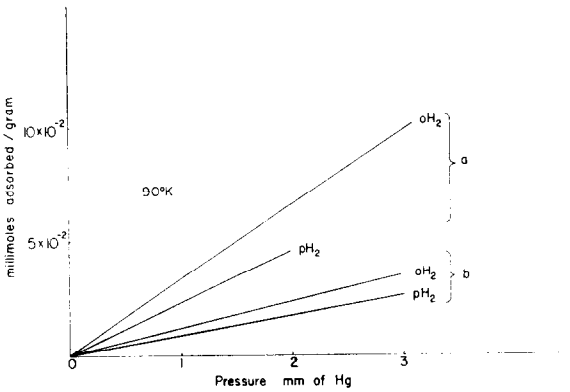

FIG. 6. Adsorption isotherms on molecular sieve 13X, 90°K, calculated from (a) Fig. 1, (b) Fig. 2.

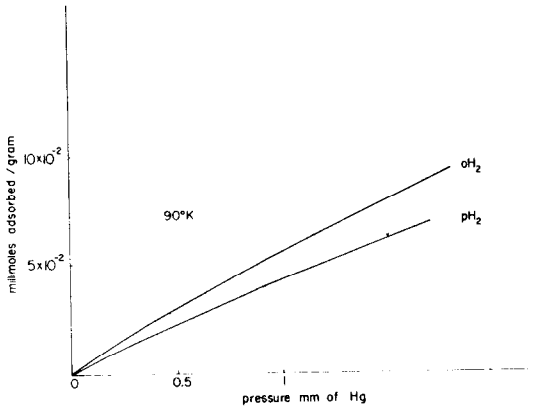

FIG. 7. Adsorption isotherms on molecular sieve 5A.

This value depends on the amount of the sample if the isotherms are not linear. It is, therefore, necessary to relate the data to the same charge. Then we obtain if, for example, $a = 1.5 \times 10^{-3}$ mmole/g,

$$T = 90°\text{K} \qquad \Delta G = 72 \text{ cal}$$

$$T = 77°\text{K} \qquad \Delta G = 92 \text{ cal}$$

Between $a = 1.5 \times 10^{-3}$ mmole/g and $a = 6 \times 10^{-2}$ mmole/g the ΔG-values were equal within the limit of error.

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