

and this too is persistent. If as has been supposed, these maxima are attributable to  $2^3P_0$  and  $2^3P_1$  states of the molecule respectively, it is clear that persistence cannot be peculiar to the states which in the atom are metastable, but occur also in the  $2^3P_1$  molecule.

Incidentally, it is shown that self-luminous mercury vapour issuing through a nozzle from a region of high to low pressure, with the velocity of sound, shows very beautifully the stationary vibrations which are usually investigated by a shadow method, using an air jet.

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### *On the Refractivity of Para-Hydrogen.*

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In the paper by K. F. Bonhoeffer and P. Harteck\* published in 1929, on para-hydrogen, no mention is made of the refractive index of the new modification, and, so far as we can find, no experiments on this subject have hitherto been published. It may, therefore, be presumed that, on the hypothesis which led to the discovery of the para-form, no change of index was expected; and, on any theory, it seemed probable that the change would be very small. It appeared worth while, however, to make use of a Jamin interferometer already set up for other purposes to test this point experimentally and the following paper records the result of the investigation.

Para-hydrogen was prepared by adsorbing ordinary hydrogen, purified by previous adsorption in palladium, in charcoal at the temperature of liquid oxygen ( $-183^\circ \text{C}.$ ). After  $1\frac{1}{2}$  to 2 hours the gas was allowed to warm up, and should then consist of approximately 50 per cent. ortho- and 50 per cent. para-hydrogen. In order to test whether this was actually so Schleiermacher's method of measuring the thermal conductivities of the two forms, as described in Bonhoeffer and Harteck's paper, was followed. In their case a Wollaston wire (0.01 mm. diameter) was stretched in a narrow cylindrical tube immersed in liquid hydrogen, and the change in the resistance of the wire, which was electrically heated to  $200^\circ$  absolute, was observed when para- was substituted for ordinary hydrogen at the same pressure (40 mm.). In these circumstances the resistance varied between 111.85 ohms for ordinary hydrogen to 106.25 for hydrogen containing 99.7 per cent. para-hydrogen.

\* 'Z. phys. Chem.,' B., vol. 4, p. 113 (1929).

When liquid air was used for cooling both the charcoal and the measuring tube the resistance varied from 112.96 ohms for ordinary hydrogen from a cylinder to 111.13 for a mixture containing about 50 per cent. para-hydrogen, a change of 1.62 per cent.

In our apparatus the diameter of the wire was 0.02 mm. and in other respects the dimensions were different from those of Bonhoeffer and Harteck. Liquid hydrogen not being readily available liquid oxygen was employed, and the resistance of the wire was measured over a range of pressures from 2 to 10 cm. The resulting graphs of resistance plotted against pressure, though not pretending to a high degree of accuracy showed a reduction of resistance, when the adsorbed gas was substituted for ordinary hydrogen, of 1 part in 70, or 1.43 per cent. Whether the difference between this ratio and that obtained by Bonhoeffer and Harteck (1.62) is due to differences in the dimensions of our apparatus or to failure to obtain as high a percentage of para-hydrogen as they did we do not decide. Possibly the use of liquid oxygen instead of liquid air accounts for the difference. But, in any case, our values indicate the presence of about 47 per cent. of para-hydrogen in the gas employed, and this sufficed for our purpose.

In the refractivity measurements freshly prepared para-hydrogen 47/53 was allowed to warm to the temperature of the room and measurements were immediately made of its refractive index. The refractometer tubes were 103.9 cm. long, the approximate pressure change during an experiment was 35 cm. of mercury and the approximate number of bands counted 120. With these data, and with pressures read to 0.1 mm., temperatures to 0.1° C. and bands to 0.1 it should be possible to measure the refractivity of a gas to 1 part in 1400, *i.e.*, to determine the fourth significant figure of the refractivity (0.0001396). To obtain the fifth figure accurately would involve an amount of labour incommensurate with the present value of the result; but by taking the mean of a number of experiments a fair approximation may be obtained.

The refractivity of ordinary hydrogen has often been measured, and some of the more recent results for the green mercury line are shown below:—

| Date. | Observer.                   | ( $\mu - 1$ ) $10^8$ . |
|-------|-----------------------------|------------------------|
| 1896  | Perreau .....               | 13925                  |
| 1907  | Scheel .....                | 13916                  |
| 1909  | C. and M. Cuthbertson ..... | 13971                  |
| 1912  | J. Koch .....               | 13966                  |
| 1921  | Kirn .....                  | 13965                  |
| 1923  | Schackerl .....             | 13965                  |



From these figures it appears certain that the true value lies between  $(1396)10^{-7}$  and  $(1397)10^{-7}$  and J. Koch's value  $(13966)10^{-8}$  may be accepted as very nearly correct.

Numerous observations were made by us, both with the short glass tubes mentioned above and with brass tubes (length  $274.06$  cm.) previously used for measuring the refractive index of neon. For ordinary hydrogen the mean of 14 double experiments (pressure falling and rising) was  $(13964)10^{-8}$ , a result sufficiently near to Koch's value to test the accuracy of the experimental arrangements and the purity of the gas.

For freshly prepared para-hydrogen a preliminary series of 14 double experiments gave the mean value of  $(13971)10^{-8}$ . A final series of six experiments, which we consider much more trustworthy than the preliminary series, gave the following values :—

| $(\mu - 1)10^8.$ |      | $(\mu - 1)10^8$ |
|------------------|------|-----------------|
| 13963            |      | 13971           |
| 13963            |      | 13960           |
| 13977            |      | —               |
| 13959            | Mean | 13965           |
|                  |      | —               |

The difference between this value and Koch's value for ordinary hydrogen is within the limits of experimental error, and we conclude that if there is any difference between the refractivities of ordinary hydrogen and hydrogen recently adsorbed in charcoal at the temperature of liquid oxygen, and containing about 47 per cent. of para-hydrogen it does not exceed 2 or 3 parts in 14,000.

In these experiments the gas came into contact with mercury, tap grease, brass (in the early experiments) and cotton wool (in the bore of a tap). The light used was a mercury arc in quartz, but covered by a thick glass plate.

It was, therefore, necessary to enquire whether any of these materials could have retransformed the para-hydrogen into ordinary hydrogen before the refractivity measurements could be completed and so rendered the experiments futile.

With regard to the mercury arc Senftleben\* states that, in the presence of a trace of mercury, irradiation by the mercury line ( $\lambda$  2537) quickly transforms para- to ortho-hydrogen. Glass is opaque to this wave-length, but in order to test whether any of the light to which it is transparent could have had the same

\* 'Z. phys. Chem.,' vol. 4, p. 169 (1929).

effect in our experiments a thermal conductivity experiment was made, first with freshly prepared para-hydrogen and, later, with the same gas after it had been illuminated by the shielded mercury arc for 15 minutes. No change of resistance in the wire was observed.

The absence of any catalytic effect in cotton wool was proved by allowing the gas used in one of the refractivity experiments to flow into the tube without passing through the tap in question. No difference was observed. The possible influence of brass tubes is disposed of by the observation that the early series of experiments with brass tubes did not give different results from those in which brass was not used.

Tap grease was evidently used in the German experiments without detrimental results, and the gas used in our thermal conductivity experiments, which gave positive results, passed through two or three greased taps.

It was considered whether it would be desirable to repeat these experiments with gas adsorbed in charcoal at the temperature of liquid hydrogen, containing 99.7 per cent. of para-hydrogen. But in the absence of any positive result in this research it was not thought worth while to pursue the matter further at present.

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### *Summary.*

Para-hydrogen was prepared by adsorption of pure hydrogen in charcoal at the temperature of liquid oxygen, and the refractive index of a mixture of about 47 per cent. para- to 53 per cent. ortho-hydrogen was measured.

It was found that, at the temperature of the room, for the green mercury line, the index does not differ from that of ordinary hydrogen. The limits of error of the experiments were about 3 parts in 14,000.

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