Exchange between Hydrogen and Deuterium on Charcoal

By *R. Burstein*

In their investigation of the temperature dependence of the rate of the para-ortho hydrogen conversion Bonhoeffer, Farkas and Rummel[1] concluded that at low temperatures this process takes place on account of the paramagnetic properties of the charcoal surface, and at high temperatures, by means of the decomposition of the hydrogen molecule into atoms.

However, measurements of the activation energy of the low-temperature and high-temperature conversion have shown that the energy of activation of the two processes is the same [2].

In order to elucidate the mechanism of the para-ortho-conversion on charcoal the author has investigated the reaction of exchange between hydrogen and deuterium as an example of a reaction that can only proceed by way of an interaction of the two molecules.

The apparatus in which these experiments were carried out has been described in one of the preceding papers [3], the only difference being that instead of the vessel *M*, in which a platinum wire had been stretched, a quartz vessel containing five grams of charcoal was used. Before beginning the experiment, the charcoal was subjected to prolonged degasing at 900 — 950°C, the activity of the charcoal increasing as the degasing proceeded and becoming constant only after a month's degasing.

The measurement of the kinetics of the exchange was made by the modified method of Farkas previously described [3], *i. e.*,

[1] Bonhoeffer, Farkas a. Rummel, Z. physik. Chem., B **21** 225 (1933).
[2] Acta Physicochimica URSS, **1**,465 (1934). Trans. Farad. Soc., **32**, 823 (1936).
[3] R. Burstein, Acta Physicochimica URSS, **6**, 815 (1937).

under a pressure of the gas of 12—15 mm., at a temperature of the filament of 170° K, and a temperature of the wall of 90° K. The experiments were made with a 50 per cent. mixture of $H_2 + D_2$.

The gas was passed through the charcoal by means of a circulation pump. The measurement of the kinetics of the para-ortho-conversion was made by the same method.

The exchange between hydrogen and deuterium and the para-ortho-conversion were investigated at different temperatures. In order to elucidate the rôle of active centres in the exchange reaction, the relation between the reaction velocity and the amount of hydrogen adsorbed at 500°C was investigated by a method similar to that used in the previous investigations of the kinetics of the para-ortho-conversion of hydrogen [2].

Table 1

$H_2 + D_2$

T°K	Time of half exchange in seconds
193	90
300	120
500	120
90 stat.	120
para-ortho 300	40

A study of the exchange reaction showed that this reaction takes place on well-degased charcoal, the rate of exchange at temperatures of 190°K, 300°K and 500°K being practically the same. The time of half-exchange at various temperatures is given in Table 1. It should be noted that at 500°K the reaction is self-poisoned and therefore the values given in the table have been calculated from the results obtained 1 min. after the beginning of the reaction.

These data show that the exchange reaction on a charcoal surface proceeds practically without activation energy, similarly to the reaction of the para-ortho-conversion of hydrogen, where the energy of activation in the temperature range from 190° to 300°K does not exceed 200 cals.

The exchange between hydrogen and deuterium was investigated also at 90°K. In this case the preparation of the 50 per cent. mixture was made as follows: H_2 and D_2, each separately, were adsorbed on charcoal at 90°K and brought to a state of equilibrium with respect to the para-ortho-modifications of hydrogen. Then the two gases were mixed, and the resistance of the filament was

measured in this mixture to give the composition of the mixture.

The kinetics of the exchange between H_2 and D_2 in this mixture was studied by the static method at 90°K. These experiments showed that at 90°K an exchange between hydrogen and deuterium takes place, the time of half-exchange being equal to 2 min. These data, of course, cannot be compared with those obtained at higher temperatures since at 193° and above the circulation method was

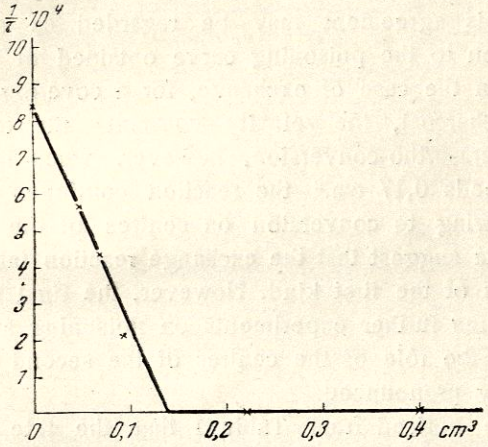

Fig. 1.

used. However, they show that the exchange between hydrogen and deuterium on charcoal at 90°K proceeds at a rapid rate.

The exchange reaction between hydrogen and deuterium on charcoal at room temperature was found to be poisoned by the hydrogen adsorbed at 500°C. These experiments were made as follows. The charcoal was degased at 900—950°, then cooled to 500°C, and at this temperature a definite amount of hydrogen was adsorbed. The charcoal was then cooled to room temperature, and the exchange reaction took place. These experiments showed that the velocity constant falls with an increase in the quantity of hydrogen adsorbed on the charcoal. The results expressing the relation between the velocity constant and the amount of hydrogen required for poisoning the surface of the charcoal are shown in Fig. 1. As can be seen from these data, the relation between the

velocity constant and the amount of hydrogen required for the poisoning of the charcoal is a linear one, the quantity of hydrogen required for the complete poisoning of the surface being 0,14 cm.^{3} for 1 gr. of charcoal. These results are similar to those obtained in the case of charcoal poisoning by hydrogen during the reaction of the para-ortho-conversion of hydrogen [2]; in the latter case the amount of hydrogen necessary for poisoning the centers of the first kind was 0,17 cm.^{3} for 1 gr. of charcoal. Considering that the reactions in the two cases were studied on charcoal of different activations, this agreement may be regarded as satisfactory. In contradistinction to the poisoning curve obtained for the para-ortho-conversion [2], in the case of exchange, for a covering of 0,14 cm.^{3} per 1 gr. of charcoal, the velocity constant falls to zero. In the case of the para-ortho-conversion, however, when the covering of hydrogen exceeds 0,17 cm.^{3} the reaction continues to proceed at a slow rate owing to conversion on centres of the second kind.

These data suggest that the exchange reaction takes place only on the centres of the first kind. However, the final settling of this question requires further experiments on poisoning at lower temperatures where the rôle of the centres of the second kind becomes more distinctly pronounced.

It will be noticed from Table 1 that the rate of the para-ortho-conversion is about three times as high as that of the exchange reaction.

In order to elucidate the nature of the active centres and to settle the question whether their presence in the charcoal is connected with the ash content in sugar charcoal (0,02 per cent.), exchange tests were undertaken on carbolite charcoal prepared by condensing thrice-distilled formalin and phenol.

The carbolite produced in this way was charred and then activated by burning 50 per cent. of its original quantity. This charcoal contained 0,003 per cent. of ash.

In degasing carbolite charcoal it was found that it contains a large amount of hydrocarbons, the removal of which from the surface of the charcoal even at 1000°C proceeds at a slow rate. A black coating is formed on the walls of the quartz vessel over the furnace owing to the decomposition of the hydrocarbons during the degasing. After degasing for a month the kinetics of the

exchange and of the para-ortho-conversion of hydrogen on this charcoal were measured, and the velocity of the two reactions was found to be fifteen times less than the corresponding reaction rates on sugar charcoal.

Further degasing little increased the activity of the charcoal. In order to purify the surface of the charcoal from the hydrocarbons left, the charcoal was exposed to air at room temperature for 15 hours and then degased at 1000°C for 48 hours. After this treatment the rate of exchange on carbolite charcoal at 300°K became three times as high (time = 40 seconds) as that on sugar charcoal.

Experiments on the poisoning of carbolite charcoal showed that the number of active centers on this charcoal is greater than on sugar charcoal. Thus, in the case of sugar charcoal, for a decrease of $\frac{1}{\tau}$ from $8{,}33 \cdot 10^{-3}$ to $4{,}02 \cdot 10^{-3}$, 0,074 cm.³ of hydrogen were required, while in the case of carbolite charcoal, in order to obtain the same velocity constant $4{,}02 \cdot 10^{-3}$, 0,21 cm.³ were needed.

Discussion of results

The reaction between hydrogen and deuterium on the surface of charcoal was studied by A. Farkas and L. Farkas[4], and by J. Gould, W. Bleakney and H. Taylor[5]. These authors found that the reaction between hydrogen and deuterium on charcoal does not take place. In the light of the present data, this fact may be accounted for as being due to insufficient degasing of the charcoal.

In the work of J. Gould, B. Bleckney and H. Taylor[6] the degasing was made at 400°C. Under these conditions a large amount of adsorbed gases is left on the charcoal surface, and they poison the active centers on the surface of the charcoal. From the experiments described above it can be seen that up to 90°K an exchange between hydrogen and deuterium does indeed take place on a charcoal surface.

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[4] A. Farkas a. L. Farkas, Nature, **132**, 894 (1933).
[5] J. Gould, W. Bleakney a. H. Taylor, J. Chem. Phys., **2**, 362 (1934).
[6] H. Taylor, J. Chimie Physique, **34**, 529 (1937).

This reaction takes place on charcoal at temperatures at which only van der Waals' adsorption is observed. The existence in this temperature range of an exchange reaction which proceeds only by way of an interaction of two molecules of $H_2 + D_2$ is incomprehensible, since charcoal is not a catalyst for reactions of hydrogenation. The fact of the existence of the reaction at 90° K was observed by Taylor on chromium oxide, nickel[5] and zinc oxide[6]. In the last case as well as on charcoal the exchange reaction proceeds without activation energy at low temperatures.

The kinetics of the exchange between hydrogen and deuterium obeys the equation:

$$K = \frac{1}{t} \lg \frac{\alpha}{\alpha - x},$$

where α is the concentration of HD in the equilibrium mixture (47,5 per cent.) and x is the concentration of HD after time t, *i. e.*, the equation of a reversible monomolecular reaction. The validity of this equation can be seen from Tables 2,2a.

Table 2

Date of experiment	Time in seconds t	Pure charcoal	
		x in % HD	$K \cdot 10^3$
5/VI	150	28,0	2,6
	270	39,2	2,8
	360	42,0	2,6
2/X	60	14,0	2,5
	120	23,5	2,5
	240	33,3	2,1
	300	35,3	2,0

Table 2a

Charcoal which had adsorbed 0,1 cm³. H_2 at 500° C

Time (t) in seconds	x in % HD	$K \cdot 10^4$
120	7,0	5,7
180	10,0	5,7
240	13,2	5,9
300	16,1	6,0
360	18,2	5,7
480	22,8	5,9
660	27,2	5,6
840	31,0	5,6
940	33,4	5,6
1 200	36,9	5,4

In this Table the velocity constant of the exchange of H_2 and D_2 for pure charcoal and charcoal which had adsorbed 0,1 cm.³ of hydrogen per 1 gr. of charcoal has been calculated from this equation.

The monomolecular nature of this reaction is also evidenced by the linearity of the relation between the velocity constant and the amount of hydrogen required for the poisoning of the surface of charcoal. The nature of the poisoning curves suggests that the reaction of exchange and para-ortho-conversion at the centers of the first kind proceed according to the same mechanism. These facts diminish the probability of the hypothesis of a paramagnetic mechanism of the para-ortho-conversion of hydrogen at the active centres of the first kind. On the basis of the monomolecular nature of this reaction it may be presumed that the exchange takes place by way of an interaction between adsorbed molecules and the molecules in the gaseous phase.

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