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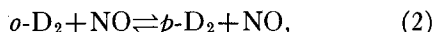
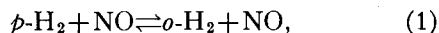
On the Paramagnetic Conversion of Parahydrogen and Orthodeuterium in the Presence of Nitrous Oxide (The Magnetic Moment of the Deuteron)

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THE present communication deals with the comparison of the rates of the two reactions



in which the *ortho-para* conversion takes place under the influence of the inhomogeneous magnetic field of the NO molecules.¹ According to the theory of Wigner² the ratio of the velocities of these two reactions is proportional to $(\mu_H/\mu_D)^2$ where μ_H and μ_D denote the magnetic moments of the proton and of the deuteron.³ In a previous paper the rate of conversion of light and heavy hydrogen was determined under the influence of O_2 ⁴ and on the basis of a theory of Kalckar and Teller⁵ the value $\mu_H/\mu_D = 4$ was obtained.

It seemed interesting to determine the ratio of the rates of conversion also under the influence of other paramagnetic substances and the reactions (1) and (2) seemed suitable for such an investigation, the comparison of the two reactions being possible in a wide temperature range.

The reaction vessel had a volume of 50 cc and was kept at constant temperature by means of an electric furnace or suitable cooling bath. First *p*-H₂ or *o*-D₂ of 20–40 mm pressure was introduced into the reaction vessel; afterwards NO of known pressure. The pressure was measured with a mercury manometer attached to the glass tube leading to the reaction vessel. *p*-H₂ and *o*-D₂ were prepared in the usual way by adsorption on charcoal, cooled with solid air. NO was prepared from a solution of potassium iodide and nitrite and fractionated in vacuum several times. The determination of the concentration of *p*-H₂ and *o*-D₂ was carried out accord-

ing to the micro-thermoconductivity method,⁶ extracting small samples from the reaction vessel by means of a capillary lock. The pressure in the reaction vessel did not change more than 1–2 per cent during a run, even if several samples were extracted from it for the analysis. Special precaution was taken to prevent NO from coming into the conductivity cell: the hydrogen NO mixture which had to be analyzed passed very slowly through a trap cooled with solid air before it was pumped into the conductivity cell.

The *ortho-para* conversion under the influence of paramagnetic substances is a bimolecular reaction. Since the pressure of the paramagnetic substance remains constant, the progress of the reaction is given by

$$u_t = u_0 e^{-k[\text{NO}]t}, \quad (3)$$

where u_t and u_0 are the excess concentration of *p*-H₂ or *o*-D₂ above the equilibrium concentration at the time $t=t$ and $t=0$ and the temperature T° abs. The half-lifetime τ of the reaction is inversely proportional to the pressure of NO and is independent of the hydrogen pressure. In Fig. 1 one experiment on the conversion of *p*-H₂ and one on the conversion of *o*-D₂ in the presence of NO are represented. It will be recognized that the conversion of *p*-H₂ is much quicker than that of the *o*-D₂ at the same pressure of NO.

In Table I the data of the experiments on the rate of the reaction (1) at different pressures and temperatures are listed. Table II gives a summary of the results obtained for the reaction (2). Each constant is the mean value obtained from a run. The velocity constants are independent of the pressure and only slightly dependent on temperature. The velocity constants, $k_{H_2}^*$ and $k_{D_2}^*$, as listed in column 5 were calculated from the observed half-lifetimes allowing for the fact that only a certain percentage of the NO molecules are paramagnetic in the proper sense. The two

¹ L. Farkas and H. Sachsse, Zeits. f. physik. Chemie **B23**, 1 (1933).

² E. Wigner, Zeits. f. physik. Chemie **B23**, 28 (1933).

³ A. and L. Farkas and P. Harteck, Proc. Roy. Soc. **A144**, 481 (1934).

⁴ A. Farkas and L. Farkas, Proc. Roy. Soc. **A152**, 152 (1935).

⁵ Kalckar and Teller, Proc. Roy. Soc. **A150**, 520 (1935).

⁶ A. Farkas and L. Farkas, Proc. Roy. Soc. **A144**, 467 (1934).

lowest electronic states of NO are ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$, the ground level ${}^2\Pi_{1/2}$ being diamagnetic and the ${}^2\Pi_{3/2}$ level, 353 cal. above the ground level, paramagnetic. Consequently only those NO molecules are paramagnetic which are in the ${}^2\Pi_{3/2}$ state and their concentration varies with the temperature as listed in column 4.

The values for the constants of the reaction (1) differ somewhat from those given in a previous paper;¹ the present determinations seem to be more accurate.

It will be seen that the constants for the parahydrogen conversion are roughly ten times greater than the constants of the orthodeuterium conversion at the same temperature.

In Table III the velocity constants of the reactions (1) and (2) are compared at different temperatures with the corresponding constants of the parahydrogen and orthodeuterium conversion under the influence of O_2 . The ratio of the constants in the case of O_2 is approximately the same as for the conversion with NO but the absolute values of the velocity constants $k^*_{H_2}$ and $k^*_{D_2}$ in columns 3 and 4 are about 5 times greater with NO than with O_2 .

The theoretical expressions for velocity constants of the conversion (in mole lit.⁻¹ min.⁻¹)

TABLE I. $p\text{-H}_2 + \text{NO} \rightleftharpoons o\text{-H}_2 + \text{NO}$.

T° ABS.	PRES-SURE IN MM HG	τ IN MIN.	% NO PARA-MAGNETIC	k^* IN MOLE LIT. ⁻¹ MIN. ⁻¹	k IN MOLE LIT. ⁻¹ MIN. ⁻¹
193	30	29	27.5	34.7	9.6
193	17	47	27.5	37.8	10.4
193	18	45	27.5	37.5	10.3
288	24	43	34.5	34.9	12.0
288	43	24	34.5	34.9	12.0
598	47	39	41.6	33.8	14.1

TABLE II. $o\text{-D}_2 + \text{NO} \rightleftharpoons p\text{-D}_2 + \text{NO}$.

T° ABS.	PRES-SURE IN MM HG	τ IN MIN.	% NO PARA-MAGNETIC	k^* IN MOLE LIT. ⁻¹ MIN. ⁻¹	k IN MOLE LIT. ⁻¹ MIN. ⁻¹
193	80	107	27.5	3.50	0.96
193	80	107	27.5	3.50	0.96
193	112	75	27.5	3.60	0.99
292	80	124	34.5	3.63	1.25
292	94	104	34.5	3.65	1.26
292	131	72	34.5	3.80	1.31
292	192	49	34.5	3.80	1.31
600	150	110	41.6	3.03	1.26
600	189	91	41.6	3.15	1.31
600	216	87	41.6	3.41	1.42
600	237	72	41.6	3.13	1.30

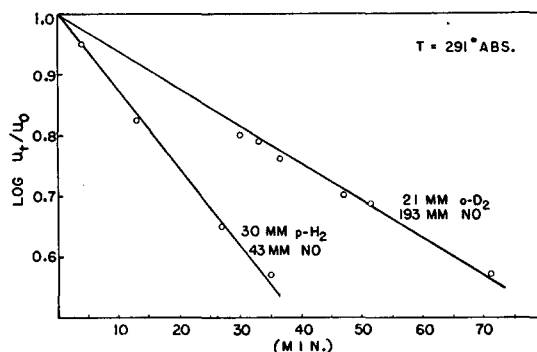


FIG. 1.

is given by

$$k = 3.6 \cdot 10^{22} d_T^2 \bar{c} \left[\frac{k_{01}a_0 + (k_{21} + k_{23})a_2 + \dots}{1 + a_2 + a_4 + \dots} + \frac{(k_{10} + k_{12})a_1 + (k_{32} + k_{34})a_3 + \dots}{a_1 + a_3 + \dots} \right], \quad (4)$$

where d_T denotes the distance of nearest approach, \bar{c} the relative velocity of the colliding molecules, k_{lm} the rate constant of the transition $l \rightarrow m$ and a_J the concentration of hydrogen molecules in the rotational state J .

According to Wigner² the theoretical expressions for the transition probabilities W_{lm} are as follows:

$$W_{J, J+1} = \frac{4\pi^2 \mu^2 \mu_X^2 I}{h^2 d_T^6 k T} \cdot \frac{1}{18} \frac{(2s+1)}{s} \frac{J+1}{2J+1} = C \mu^2 I \frac{2s+1}{s} \frac{J+1}{2J+1}, \quad (5a)$$

$$W_{J, J-1} = C \mu^2 I \frac{2s+1}{s} \frac{J}{2J+1} \quad (5b)$$

for the *ortho* \rightarrow *para* transitions,

$$W_{J, J+1} = C \mu^2 I \frac{(2s+1)(s+1)}{s^2} \frac{J+1}{2J+1}, \quad (5c)$$

$$W_{J, J-1} = C \mu^2 I \frac{(2s+1)(s+1)}{s^2} \frac{J}{2J+1} \quad (5d)$$

for the *para* \rightarrow *ortho* transitions.

In these formulae s denotes the mechanical momentum of the H or D ($s_H = \frac{1}{2}$, $s_D = 1$) nucleus, μ_X the magnetic moment of the para-

TABLE III.

T °ABS.	O ₂		NO			
	k _{H₂}	k _{D₂}	k _{H₂} *	k _{D₂} *	k _{H₂}	k _{D₂}
	IN MOLE LIT. ⁻¹ MIN. ⁻¹					
83	2.7	0.5	—	—	—	—
193	7.1	0.7	37.0	3.50	10.0	0.96
293	8.2	0.83	34.9	3.75	12.0	1.30
600	12.1	—	33.8	3.20	14.1	1.35

magnetic molecule, μ the magnetic moment of the proton or deuteron and I the momentum of inertia of the hydrogen isotope considered. For calculating the rate constants from these transitions probabilities it is the simplest to assume that $k_{lm} = W_{lm}$ if the transition is exothermic and $k_{lm} = W_{lm} \cdot e^{-(E_l - E_m)/kT}$ in case the transition of the energy level E_l to E_m is endothermic.

Introducing the values for a_J and k_{lm} into the formula (4) we obtain for rate constants

$$k_{H_2} = 3.6 \cdot 10^{22} \frac{2 \mu^2 \mu_X^2 I_{H_2} \pi^2}{9 h^2 d_T^6 kT} \left(\frac{8RT(M_{H_2} + M_X)}{\pi M_{H_2} M_X} \right)^{\frac{1}{2}} \cdot \left[\frac{12(e^{-E_1/RT} + 2e^{-E_2/RT} + 3e^{-E_3/RT} + \dots)}{\sum_{J=\text{odd}} (2J+1)e^{-E_J/RT}} + \frac{4(e^{-E_1/RT} + 2e^{-E_2/RT} + \dots)}{\sum_{J=\text{even}} (2J+1)e^{-E_J/RT}} \right], \quad (6)$$

$$k_{D_2} = 3.6 \cdot 10^{22} \frac{2 \mu^2 \mu_X^2 I_{D_2} \pi^2}{9 h^2 d_T^6 kT} \left(\frac{8RT(M_{D_2} + M_X)}{\pi M_{D_2} M_X} \right)^{\frac{1}{2}} \cdot \left[\frac{3(e^{-E_1/RT} + 2e^{-E_2/RT} + \dots)}{\sum_{J=\text{even}} (2J+1)e^{-E_J/RT}} + \frac{6(e^{-E_1/RT} + 2e^{-E_2/RT} + \dots)}{\sum_{J=\text{odd}} (2J+1)e^{-E_J/RT}} \right]. \quad (7)$$

In the communication of Farkas and Sachsse¹ it was tentatively suggested that the comparatively high rate of conversion in the presence of nitrous oxide is due to resonance between the energy of the 0→1 transition (337.2 cal.) and the energy of paramagnetic $^2\Pi_{3/2}$ level (353 cal.) of nitrous oxide. From the formula (4) it is evident

that the contribution of transition 0→1 will be large, were it not counteracted by the endothermicity of this transition. It was suggested that this energy might be preferentially supplied by paramagnetic nitrous oxide molecules.

In the light of the present experiments this view cannot be upheld. In the case of *o*-D₂ such a resonance between the energy of the first rotational state (in this case 170.2 cal.) and the energy of the $^2\Pi_{3/2}$ level of nitrous oxide does not exist and yet the rate of conversion induced by nitrous oxide is five times larger than with oxygen. This is due either to a higher specific activity of the nitrous oxide in inducing the *ortho-para* conversion for which no theoretical reason can be given at present or to the contribution of nitrous oxide molecules in the $^2\Pi_{1/2}$ state. Though this level appears in magnetic measurements as diamagnetic it might be of the same effect for an *ortho-para* conversion as the paramagnetic $^2\Pi_{3/2}$ state. Accordingly, in column 6 of Tables I and II and columns 6 and 7 in Table III the velocity constants are calculated under the assumption that all the NO molecules are equally effective for the conversion. The velocity constants thus obtained are only slightly larger than the corresponding rate constants for oxygen.

As already mentioned, on the basis of the theory of Kalckar and Teller, the value $\mu_H/\mu_D \sim 4$ was obtained from the velocity of the *p*-H₂ and *o*-D₂ conversion in the presence of O₂, according to the general formula

$$\frac{k_{H_2}(2T)}{k_{D_2}(T)} = \frac{\mu_H^2 S_D^2 (2S_H + 1) [\xi(S_H + 1) + S_H]}{2\mu_D^2 S_H^2 (2S_D + 1) [S_D + 1 + \xi S_D]}, \quad (8)$$

where $k_{H_2}(2T)$ and $k_{D_2}(T)$ are the velocity constants at the temperatures $2T$ and T and

$$\xi = \frac{\sum_{J=\text{odd}} (2J+1)e^{-E_J/RT}}{\sum_{J=\text{even}} (2J+1)e^{-E_J/RT}}.$$

This formula was derived without making special assumptions on the mechanism of the collision and compares the velocity of the *p*-H₂ conversion at the temperature $2T$ with the D₂ conversion at the temperature T , because under these conditions the momentum distribution of hydrogen and of deuterium are identical. How-

ever, Kalckar and Teller's theory neglects the influence of the kinetic energy of colliding particles on the distance of nearest approach, d_T .

According to Wigner's theory the ratio μ_H/μ_D is obtained by dividing Eq. (6) by (7).

In Tables IV and V the ratio is listed for different temperatures as calculated according to the two theories.

It will be recognized that according to Wigner's theory the same value is obtained for μ_H/μ_D from the experiments with O_2 as from experiments with NO. The formula of Kalckar and Teller gives different values. This result does not, however, invalidate the theory of Kalckar and Teller, since their basic assumptions are not fulfilled in the case of the conversion with nitrous oxide, the energy distribution of the nitrous oxide molecule not being the same at the temperature $2T$ and T .

The difference between the value for μ_H/μ_D obtained in the case of O_2 according to the theory of Teller and Kalckar on the one hand and the value for μ_H/μ_D in the cases O_2 and NO according to the theory of Wigner on the other hand is not very much. It is difficult to decide which of the two theories is the better approximation. We would like to call attention to the fact that Wigner's theory allows for the temperature variation of the distance of nearest approach, which, as pointed out in a previous paper,⁷ is quite considerable. On the other hand, the method of Kalckar and Teller allows properly for the variation of the rotational energy of H and D with temperature.

The value 3.8 for the ratio μ_H/μ_D together with the latest value for $\mu_H = 2.46$ nuclear mag-

TABLE IV. According to Wigner.

T	O_2 μ_H/μ_D	NO μ_H/μ_D
86	3.6	—
195	3.9	3.8
290	3.8	3.6
600	—	3.8
	mean	3.80

TABLE V. According to Kalckar and Teller.

T	O_2 μ_H/μ_D	NO μ_H/μ_D
86	3.85	—
195	4.03	3.35
290	4.07	3.2

netons, according to Estermann, Simpson and Stern,^{8, 9} gives for $\mu_D = 0.65$ nuclear magnetons. These values are markedly different from the results of Kellogg, Rabi and Zacharias.¹⁰ These authors obtained for $\mu_D = 2.85$ n.m. and for $\mu_D = 0.85$ n.m. and thus for the ratio $\mu_H/\mu_D = 3.35$ by measuring the deflection of hydrogen and deuterium atom beams in a magnetic field. Though it is possible that the disagreement between the values for the proton's magnetic moment according to the two methods is due to some experimental error, it is more probable that in Rabi and co-workers' experiments a hitherto unknown spin-spin interaction of the proton-electron is measured as well¹¹ and is responsible for the higher values for μ_H and μ_D . The present experiments should be compared with the measurements of Estermann and Stern, since they concern the magnetic behavior of the molecule in an external field. If we assume that the present value for $\mu_D = 0.65$ n.m. is the magnetic moment of the deuteron without the spin-spin interaction of the proton-electron, then it seems that this effect increases the value of μ_H by 0.4 n.m. and the value of μ_D by 0.2 n.m.

⁷ Farkas and Sachsse, reference 1. The variation of d with the temperature is given by

$$d_T = d_{0H_2}(1 + C_{H_2}/T)^{\frac{1}{2}} + d_{0X}(1 + C_X/T)^{\frac{1}{2}},$$

where C_{H_2} and C_X denote the Sutherland constants of H_2 and the molecule X .

⁸ I. Estermann, O. C. Simpson and O. Stern, Phys. Rev. **52**, 535 (1937).

⁹ I. Estermann and O. Stern, Phys. Rev. **45**, 761 (1934).

¹⁰ J. M. B. Kellogg, I. I. Rabi and I. R. Zacharias, Phys. Rev. **50**, 472 (1936).

¹¹ G. Breit, Phys. Rev. **51**, 248 (1937), footnote 14; L. A. Young, Phys. Rev. **52**, 138 (1937).