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# EXCHANGE REACTION BETWEEN AMMONIA AND DEUTERIUM

By

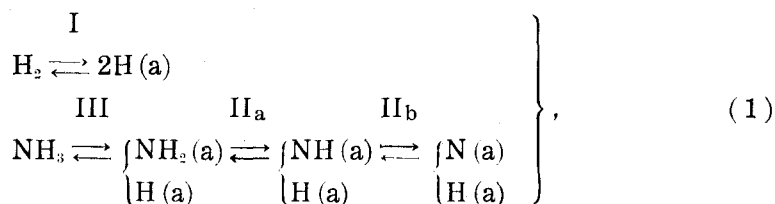
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## § 1. Introduction

KEMBALL<sup>1) 2)</sup> has observed the catalytic exchange between ammonia and deuterium on various metallic films of Ni, Fe *etc.* and found that the rate of formation of different deuterioammonias are quantitatively identical for all metals with reference to time scales appropriate to each metal.

In the present paper the above rates at the initial stage of the catalytic exchange are deduced from the dissociative scheme,

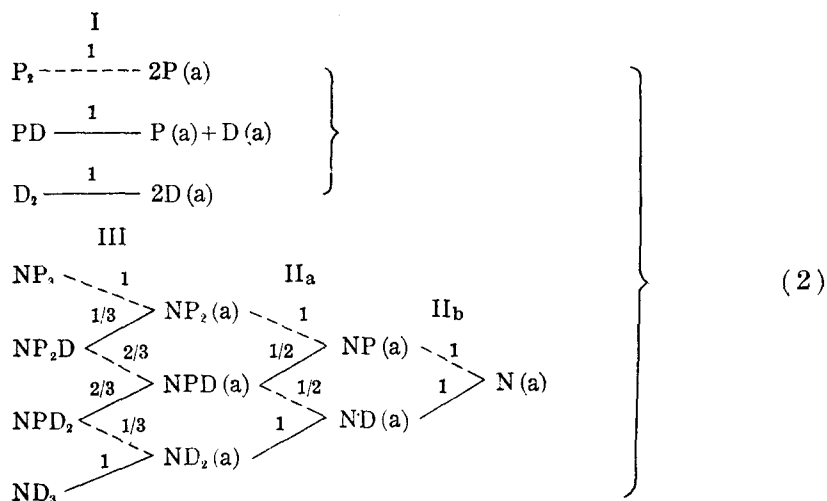


where H stands for protium P and deuterium D, by the similar method of analysis to those in the previous papers.<sup>3)</sup> The results obtained are discussed with reference to the previous one of the catalytic exchange between hydrogen and deuterioammonia<sup>4)</sup> and to the mechanism of catalytic synthesis or decomposition of ammonia.<sup>5) 6)</sup>

## § 2. Calculation

Scheme (1) may be developed discriminating between P and D as

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where the dotted or full line denotes the transfer of P or D respectively and annexed number indicates the fraction of the rate of dissociation specified by the line, of the atom group on its left over the total rate of dissociation of the same atom group, identifying the kinetic behaviour of D with that of P.

The rate of formation of every atom group in the Scheme (2) is now given as

$$\left. \begin{array}{l}
 V^{\text{P}_1} = V(\text{I}) \{ (y^{\text{P}_1})' - y^{\text{P}_1} \} \\
 V^{\text{PD}} = V(\text{I}) \{ 2y^{\text{P}}y^{\text{D}} - y^{\text{PD}} \} \\
 V^{\text{D}_1} = V(\text{I}) \{ (y^{\text{D}_1})' - y^{\text{D}_1} \}
 \end{array} \right\} \quad (3. a)$$

$$\left. \begin{array}{l}
 V^{\text{NP}_1} = V(\text{III}) (y^{\text{NP}_1}y^{\text{P}} - y^{\text{NP}_1}) \\
 V^{\text{NP}_2\text{D}} = V(\text{III}) (y^{\text{NP}_2}y^{\text{D}} + y^{\text{NPD}}y^{\text{P}} - y^{\text{NP}_2\text{D}}) \\
 V^{\text{NPD}_2} = V(\text{III}) (y^{\text{NPD}}y^{\text{D}} + y^{\text{ND}_2}y^{\text{P}} - y^{\text{NPD}_2}) \\
 V^{\text{ND}_3} = V(\text{III}) (y^{\text{ND}_2}y^{\text{D}} - y^{\text{ND}_3})
 \end{array} \right\} \quad (3. b)$$

$$\left. \begin{array}{l}
 V^{\text{NP}_2} = V(\text{III}) \left( y^{\text{NP}_2} + \frac{1}{3} y^{\text{NP}_2\text{D}} - y^{\text{NP}_2} \right) + V(\text{II}_a) (y^{\text{NP}_2}y^{\text{P}} - y^{\text{NP}_2}) \\
 V^{\text{NPD}} = V(\text{III}) \left( \frac{2}{3} y^{\text{NP}_2\text{D}} + \frac{2}{3} y^{\text{NPD}_2} - y^{\text{NPD}} \right) + V(\text{II}_a) (y^{\text{NP}}y^{\text{D}} + y^{\text{ND}}y^{\text{P}} - y^{\text{NPD}}) \\
 V^{\text{ND}_2} = V(\text{III}) \left( \frac{1}{3} y^{\text{NPD}_2} + y^{\text{ND}_2} - y^{\text{ND}_2} \right) + V(\text{II}_a) (y^{\text{ND}}y^{\text{D}} - y^{\text{ND}_2})
 \end{array} \right\} \quad (3. c)$$

$$\left. \begin{aligned} V^{\text{NP}} &= V(\text{II}_a) \left( y^{\text{NP}_2} + \frac{1}{2} y^{\text{NPD}} - y^{\text{NP}} \right) + V(\text{II}_b) y^{\text{P}} \\ V^{\text{ND}} &= V(\text{II}_a) \left( \frac{1}{2} y^{\text{NPD}} + y^{\text{ND}_2} - y^{\text{ND}} \right) + V(\text{II}_b) y^{\text{D}} \\ V^{\text{N}} &= V(\text{II}_b) (y^{\text{NP}} + y^{\text{ND}} - y^{\text{N}}) \end{aligned} \right\} \quad (3. d)$$

where  $V(j)$  ( $j=\text{I}, \text{II}_a, \text{II}_b$  or  $\text{III}$ ) denotes the total forward or backward rate of step  $j$  balanced with each other as a whole irrespective of isotopic difference i. e. at overall equilibrium, and  $y^{\text{P}}$  the fraction of the number of P(a) over the sum of the numbers of P(a) and D(a),  $y^{\text{NP}}$ , the fraction of the number of  $\text{NP}_3$  over the sum of those of  $\text{NP}_3$ ,  $\text{NP}_2\text{D}$ ,  $\text{NPD}_2$  and  $\text{ND}_3$ , and so on.

Specializing above equations to the initial condition, i. e., that  $y^{\text{D}_2}=y^{\text{NP}_3}=1$  and  $y^{\text{P}}=y^{\text{P}_2}=y^{\text{NP}_2\text{D}}=y^{\text{NPD}_2}=y^{\text{ND}_3}=0$ , and putting rates  $V^{\text{NP}_2}$  etc. of intermediates  $\text{NP}_2$ (a) etc. individually zero for the steady state, we have

$$\left. \begin{aligned} V^{\text{P}_2} &= V(\text{I}) (y^{\text{P}})^2 \\ V^{\text{PD}} &= 2V(\text{I}) y^{\text{P}} y^{\text{D}} \\ V^{\text{D}_2} &= V(\text{I}) \{ (y^{\text{D}})^2 - 1 \} \end{aligned} \right\} \quad (4. a)$$

$$\left. \begin{aligned} V^{\text{NP}_3} &= V(\text{III}) (y^{\text{NP}_2} y^{\text{P}} - 1) \\ V^{\text{NP}_2\text{D}} &= V(\text{III}) (y^{\text{NP}_2} y^{\text{D}} + y^{\text{NPD}} y^{\text{P}} - y^{\text{NP}_2\text{D}}) \\ V^{\text{NPD}_2} &= V(\text{III}) (y^{\text{NPD}} y^{\text{D}} + y^{\text{ND}_2} y^{\text{P}} - y^{\text{NPD}_2}) \\ V^{\text{ND}_3} &= V(\text{III}) y^{\text{ND}_2} y^{\text{D}} \end{aligned} \right\} \quad (4. b)$$

$$\left. \begin{aligned} y^{\text{NP}_2} &= (1 - \alpha) + \alpha y^{\text{NP}} y^{\text{P}} \\ y^{\text{NPD}} &= \alpha (y^{\text{NP}} y^{\text{D}} + y^{\text{ND}_2} y^{\text{P}}) \\ y^{\text{ND}_2} &= \alpha y^{\text{ND}} y^{\text{D}} \end{aligned} \right\} \quad (4. c)$$

$$\left. \begin{aligned} y^{\text{NP}} &= y^{\text{NP}_2} + \frac{1}{2} y^{\text{NPD}} + \beta y^{\text{P}} \\ y^{\text{ND}} &= \frac{1}{2} y^{\text{NPD}} + y^{\text{ND}_2} + \beta y^{\text{D}} \end{aligned} \right\} \quad (4. d)$$

where

$$\alpha = \frac{V(\text{II}_a)}{V(\text{II}_a) + V(\text{III})} \quad \text{and} \quad \beta = \frac{V(\text{II}_b)}{V(\text{II}_a)}, \quad (4. a), (4. \beta)$$

and hence

$$\left. \begin{aligned} V^{\text{NP}_3} &= V(\text{III}) F_0 \\ V^{\text{NP}_2\text{D}} &= V(\text{III}) F_1 \\ V^{\text{NPD}_2} &= V(\text{III}) F_2 \\ V^{\text{ND}_3} &= V(\text{III}) F_3 \end{aligned} \right\} \quad (5. V)$$

$F_0$  etc. in above equations are the following functions of  $y^D$ ,  $\alpha$  and  $\beta$ ;

$$\left. \begin{aligned} F_0 &= (1-y^D) A_0 B_0 - 1 \\ F_1 &= (1-y^D) A_0 B_0 \left( \frac{y^D}{1-y^D} + A_1 \right) + B_1 \\ F_2 &= (1-y^D) \left\{ (A_0 A_1 B_0 + B_1) \left( \frac{y^D}{1-y^D} + A_2 \right) + B_2 \right\} \\ F_3 &= y^D \{ A_2 (A_0 A_1 B_0 + B_1) + B_2 \} \end{aligned} \right\} \quad (5.F)$$

$$\left. \begin{aligned} A_0 &= \frac{1}{a_0 - \frac{1-y^D}{2} A_1} \quad B_0 = \frac{b_0 + \frac{1-y^D}{2} B_1}{a_0} \quad a_0 = \frac{1+\beta}{\alpha} - 1 + y^D \\ A_1 &= \frac{y^D}{a_1 - (1-y^D) A_2} \quad B_1 = \frac{b_1 + (1-y^D) B_2}{a_1} \quad a_1 = \frac{1+\beta}{\alpha} - \frac{1}{2} \\ A_2 &= \frac{y^D}{2a_2} \quad B_2 = \frac{b_2}{a_2} \quad a_2 = \frac{1+\beta}{\alpha} - y^D \end{aligned} \right\}$$

$$\left. \begin{aligned} b_0 &= \frac{(1-\alpha)(1+\beta)}{\alpha} + \beta(1-y^D)^2 \\ \text{and} \quad b_1 &= 2\beta y^D (1-y^D) \\ b_2 &= \beta (y^D)^2 \end{aligned} \right\}$$

The Table below shows the values of  $y^D$ ,  $\alpha$  and  $\beta$  determined from three independent equations provided by (5. V) and the relative values,

$$-V^{\text{NP}_3} : V^{\text{NP}_2\text{D}} : V^{\text{NPD}_2} : V^{\text{ND}_3} = 1.00 : 0.88 : 0.11 : 0.01$$

common to all metals as observed by KEMBALL at 6 mmHg partial

TABLE Calculated relative rates of formation of deuteroammonias

$y^D$	$\alpha$	$\beta (= \frac{V(\text{IIb})}{V(\text{IIa})})$	Relative values of $V^{\text{NP}_3}$ , etc.				$\frac{V^{\text{NP}_3}}{V(\text{III})}$	$\frac{V(\text{III})}{V(\text{IIa})}$	$\frac{V(\text{I})}{V(\text{IIa})}$	Slowest step
			$V^{\text{NP}_3}$	$V^{\text{NP}_2\text{D}}$	$V^{\text{NPD}_2}$	$V^{\text{ND}_3}$				
0.195	0.570	0.012	-1.000	0.884	0.110	0.006	-3.110	0.755	0.165	IIb

pressures both of D and  $\text{NP}_3$ .

The value of  $V^{\text{NP}_3}/V(\text{III})=F'$  or  $V(\text{III})/V(\text{II}_a)$  in the fourth or third last column of the Table was calculated by (5.  $F'$ ) or by (4.  $\alpha$ ) respectively from the known values of  $y^{\text{D}}$ ,  $\alpha$  and  $\beta$ . The next column gives  $V(\text{I})/V(\text{II}_a)$  calculated by the equation

$$\frac{V(\text{I})}{V(\text{II}_a)} = \frac{y^{\text{D}}}{2(1-y^{\text{D}})} \left\{ 1 + \beta + \frac{1-\alpha}{\alpha} - \frac{\alpha + 2\beta(\alpha + \beta)}{2(1+\beta) - \alpha} \right\}$$

which is derived by eliminating seven quantities,  $y^{\text{NP}_3}$ ,  $y^{\text{ND}_2}$ ,  $y^{\text{NP}}$ ,  $y^{\text{ND}}$ ,  $y^{\text{P}}$ ,  $\frac{V(\text{III})}{V(\text{II}_a)}$  and  $\frac{V(\text{II}_b)}{V(\text{II}_a)}$ , from eight equations, i. e. the steady state equation for D(a) at the initial stage of the reaction,

$$y^{\text{D}} \{ 2V(\text{I}) + V(\text{II}_a) + V(\text{II}_b) + V(\text{III}) \} = 2V(\text{I}) + V(\text{II}_a) \left( \frac{1}{2} y^{\text{NP}_3} + y^{\text{ND}_2} \right) + V(\text{II}_b) y^{\text{ND}},$$

those for  $\text{NPD}$  (a),  $\text{ND}_2$  (a) and  $\text{ND}$  (a) given by (4. c) and (4. d), the relation that  $y^{\text{NP}} + y^{\text{ND}} = 1$  and  $y^{\text{P}} + y^{\text{D}} = 1$ , (4.  $\alpha$ ) and (4.  $\beta$ ).

### § 3. Discussion

1. The rates of steps are of the relative magnitudes,  $V(\text{II}_b) \ll V(\text{I}) \ll V(\text{III}) < V(\text{II}_a)$  as shown in the Table, i. e. the step  $\text{II}_b$  is very slow compared with others. This conclusion gives a positive proof for those of HORIUTI *et al.*<sup>(5) (6)</sup> for the synthesis or the decomposition of ammonia on ammonia synthesis catalyst; HORIUTI and ENOMOTO<sup>(5)</sup> have namely determined the stoichiometric number of the rate-determining step at 2 for the ammonia synthesis reaction which confines the possible rate-determining step to one of the three steps, III,  $\text{II}_a$  or  $\text{II}_b$  of Scheme (1), and HORIUTI and TOYOSHIMA<sup>(6)</sup> concluded from the analysis of the decomposition of ammonia in the presence of hydrogen that the rate-determining step is  $\text{II}_b$ .

2. It is concluded from the result of the present analysis,  $V(\text{I}) \ll V(\text{III}) < V(\text{II}_a)$ , and Scheme (1) that the increasing rate of the atomic fraction of protium in gaseous deuterium is controlled by the step I.

HORIUTI and SUZUKI<sup>(4)</sup> has observed the exchange reaction between  $\text{P}_2$  and  $\text{ND}_3$  on an annealed nickel wire at room temperatures concluding that chemisorption of hydrogen, i. e. I in this case, is the rate-determining step. The conclusion of the present analysis is in complete concordance with that of HORIUTI and SUZUKI.

The author is grateful to Prof. J. HORIUTI for his valuable discussions on this work.

### References

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- 6) HORIUTI and TOYOSHIMA, to be published shortly.

*Note added in proof.* Assuming that the formation of nitrogen in the above exchange reaction is practically negligible (no information concerning this assumption can be drawn from Kemball<sup>1,2)</sup>). The step  $N(a) \rightleftharpoons \frac{1}{2} N_2$  was not included in Scheme (1). If nitrogen gas is not formed at all,  $N(a) \rightleftharpoons \frac{1}{2} N_2$  will be rate-determining in the decomposition of ammonia in the presence of hydrogen in contradiction to § 3, 1. However, we consider for the present that the rate of the nitrogen formation is controlled by II<sub>b</sub> and hence negligibly small compared with those of deuterioammonias even if the step  $N(a) \rightleftharpoons \frac{1}{2} N_2$  be faster than II<sub>b</sub>. It is necessary to make sure of the above consideration by the simultaneous observation of the rate of the nitrogen formation in the exchange reaction.