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CATALYZED EXCHANGE REACTION BETWEEN AMMONIA AND DEUTERIUM IN THE PRESENCE OF EVAPORATED NICKEL FILM

By

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Abstract

The catalyzed exchange reaction between ammonia and deuterium on evaporated nickel film at temperatures in the neighbourhood of 100°C was followed by means of mass spectrometers, and formation rates of individual exchange products of ammonia and deuterium at the initial stage of the reaction were determined. The experimental results were analyzed, accepting that the exchange was effected by the sequence of steps, I: $H_2 \to 2H(a)$, III: $NH_3 \to NH_2(a) + H(a)$, II_a: $NH_2(a) \to NH(a) + H(a)$, II_b: $NH(a) \to N(a) + H(a)$. The relative magnitudes of rates $V(I)$ *etc.* of steps I *etc.* were thus found to be $V(I) \cong V(III) \gg V(II_a) \gg V(II_b)$, and their activation energies were calculated, neglecting $V(II_b)$ compared with the first three rates, as 14.3 kcal., 37.1 kcal. and 10.6 kcal. for steps I, II_a and III respectively. The conclusion is in conformity with some other experimental results obtained in this laboratory.

Introduction

The present author has discussed in the previous paper[1)] the formation rates of deuteroammonias observed by KEMBALL[2)] in course of the catalyzed exchange reaction in the presence of various evaporated metallic films on the basis of the reaction scheme

$$\left.\begin{array}{l} H_2 \xrightarrow{\mathrm{I}} 2H(a) \\[1em] NH_3 \xrightarrow{\mathrm{III}} \begin{cases} NH_2(a) \\ H(a) \end{cases} \xrightarrow{\mathrm{II_a}} \begin{cases} NH(a) \\ H(a) \end{cases} \xrightarrow{\mathrm{II_b}} \begin{cases} N(a) \\ H(a) \end{cases} \end{array}\right\}, \qquad (1)$$

where H stands for protium P or deuterium D. The analysis of the experimental results was not conclusive because of the lack of the simultaneous observation of the formation rates of P_2 and PD in hydrogen gas, which is required for carrying out the analysis as pointed out in the previous papers[3)].

The formation rates of P_2 and PD were now followed in the present

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experiment simultaneously with the formation rates of different deuteroammonias in the presence of evaporated nickel film at 100° and 120°C by means of two mass spectrometers each for hydrogen or ammonia, and the reaction mechanism was deduced from the results on the basis of the above reaction scheme. Some other experimental results were discussed in connection with the reaction mechanism thus deduced.

Experimental

§ 1. Materials

Deuterium: Cylinder deuterium gas of 99.5 D%*) was purified by passing it through heated platinized asbestos and a liquid nitrogen trap packed with glass wool.

Ammonia: Ammonia obtained from its concentrated aqueous solution was purified by fractional distillations under vacuum from −30° to −195°C. Deuterium and ammonia thus purified were mixed with each other at 3 : 1 mole-ratio and stored.

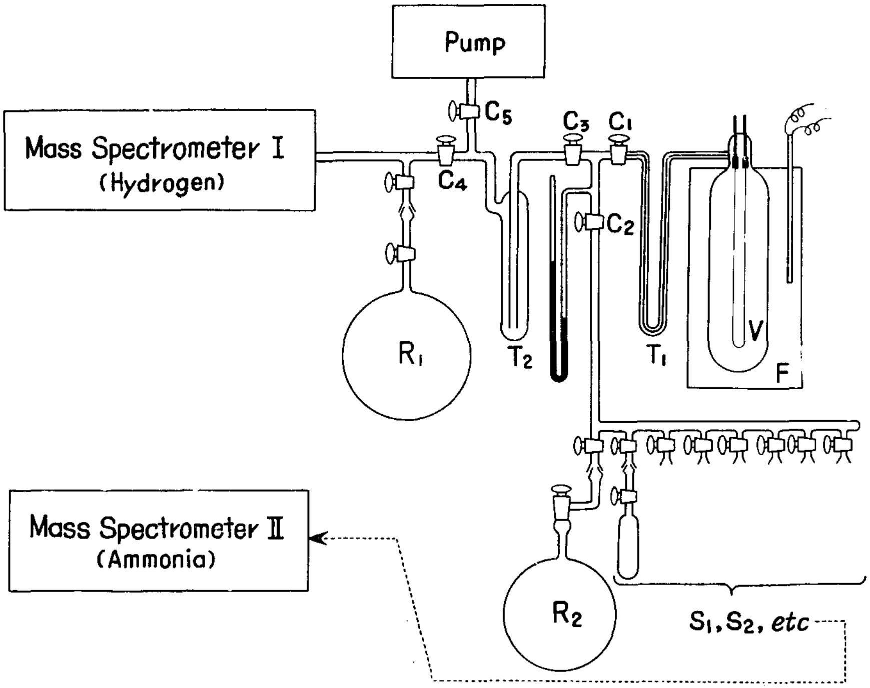

Fig. 1. Reaction apparatus.

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*) From Stuart Oxygen Co. Ltd., San Francisco.

Evaporated nickel film: A hairpin of the four-nine grade pure nickel*) wire of 0.4 mm diameter was screwed down, as shown in Fig. 1, to the nickel leads in the reaction vessel V of Hario glass**) preliminarily cleansed with bichromic acid mixture. The vessel and the wire were outgassed for two hours by heating the former with the electric furnace F at 400°C while the latter was maintained red-hot electrically. The capillary trap T_1 is now immersed in liquid nitrogen, the vessel cooled to room temperature maintaining the wire red-hot. The vessel is then immersed in ice water and the nickel evaporated at the rate of *ca.* 0.5 mg/min. from the wire now heated white-hot. The weight of the evaporated nickel film was 25 mg as determined by weighing the wire before and after the experiments.

§ 2. Reaction procedure

The reaction was conducted in three series of runs; the first or second series was carried out with the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg at 100°C or 120°C respectively and the third one with the 10 : 1-mixture of D_2 and NP_3 at 110 mmHg and 100°C.

Before the first series of runs several tens mmHg deuterium gas was introduced into the reaction vessel with its inner surface coated with the evaperated nickel film from the reservoir R_1 in Fig. 1 through the trap T_1 kept in liquid nitrogen, and then the reaction vessel was placed in the furnace F preliminarily adjusted at 100°C***). After 10 min. the bath of liquid nitrogen around the trap T_1 was replaced by that of alcohol cooled at *ca.* −80°C, the vessel evacuated for 20 min., and then the first series of runs started by introducing the 3 : 1-mixture of D_2 and NP_3 from the resevoir R_2 into the vessel at 44 mmHg and immediately closing the cock C_3. After 5 min. reaction, the resultant gas was passed into the mass spectrometer I through the liquid nitrogen trap T_2 for analysis of the relative abundances of P_2, PD and D_2 in reacted hydrogen. The gas remaining in the vessel was immediately evacuated through the cock C_5 with the cock C_4 closed. Reacted ammonia trapped in T_2 was then distilled into the sampling vessel S_1. The subsequent runs were conducted similarly each after evacuating the vessel for 20 min. The changes in the relative abundances of P_2, PD and D_2 with time were determined from the results of the repeated runs of the series with the 3 : 1-mixture at 44 mmHg, at 100°C and

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*) From Johnson Massey Co. Ltd.

**) A sort of Pyrex glass supplied by Shibata Chemical MFG. Co. Ltd., Tokyo.

***) The head of the reaction vessel with bare glass surface was kept outside the furnace in order to prevent the catalysis by the glass surface observed in a previous work (Ref. 4).

at different reaction times; the samples, S_1, S_2 *etc.* of reacted ammonia of the respective runs were analyzed by means of the mass spectrometer II.

After the completion of the first series the nickel film was reactivated by oxydizing it with *ca.* 100 mmHg air at 400°C for 30 min., evacuating subsequently for 20 min. and reducing twice with several tens mmHg D_2 at 300°C for 30 min. The vessel was then evacuated at 300°C for 10 min. and cooled to 100°C under continuous evacuation. The 3 : 1-mixture was now introduced at 44 mmHg and the exchange reaction was followed by the increase in the concentration ratio $[PD]/[D_2]$ of PD to D_2 for 5 min. at 100°C in order to check with the activity of the catalyst.

The second series was now started by raising the temperature of the furnace from 100°C to 120°C during the 20 min. evacuation subsequent to the above control experiment. The second and third series were conducted similarly under the specified conditions each followed by the control experiment described above. The temperature fluctuation of the furnace F was regulated within ±1°.

§ 3. Measurements

The mass spectrometer I mentioned above is Hitachi type RMD-3 particularly designed for analysis of the relative abundances of P_2, PD and D_2 in hydrogen gas by determining potentiometrically the ratio of any two of the three ion-currents of mass-number 2, 3 and 4; the result was corrected as described in Appendix for an appreciable amount of D^+ ion produced by ionizing electrons in the mass spectrometer.

The inner surface of the ionization chamber of the mass spectrometer was coated with gold to minimize the equilibration $P_2 + D_2 = 2PD$ catalyzed by the surface. The analyzer tube was preliminarily washed out by passing deuterium gas through it, being heated at 150°C under continuous evacuation for about a week until a constant value $(125 \pm 10) \times 10^{-4}$ of the concentration ratio $[PD]/[D_2]$ of PD to D_2 in 99.5 D % deuterium gas was obtained for 33 V accelerating voltage applied*) to ionizing electrons; every measurement was preceded by flowing deuterium gas from the reservoir R_1 through the analyzer tube for several minutes to make the memory effect uniform.

The mass spectrometer II for analysis of ammonia is the 90°-type one with magnetic scanning. Its electric circuits were operated by stabilized power-supplies except the Dubridge-Brown's one, which functioned by an 18 V accumulator. The latter circuit included an electrometer valve Toshiba UX-54B with its grid-leak resistor of $4.5 \times 10^{10} \Omega$, and its output was connected with

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*) *Cf.* Appendix.

a self-recording millivoltmeter of 2 mV full scale. The accelerating voltage applied to the ions produced in the mass spectrometer was adjusted so as to focus the mass-number 17 ion, *i. e.* NP_3^+.

An apparent voltage as low as 14 V was applied to the ionizing electrons in order to avoid the formation of fragments of ammonias, so that a mass spectrum with a single peak of the mass-number 17 ion was obtained for NP_3 as shown in Fig. 2a.

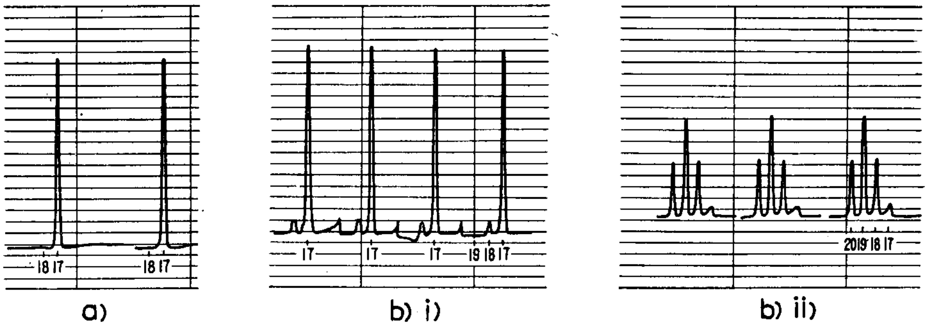


Fig. 2. Mass spectra of ammonias.

a) Mass spectrum of light ammonia with a single peak of NP_3^+.

b) Mass spectra of deuteroammonias produced by the reaction of the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg and at 100 °C; i) at the early stage and ii) at the final stage of the reaction.

Light ammonia was passed before every measurement of the reacted ammonia samples in S_1, S_2 *etc.* through the analyzer tube usually for *ca.* 10 min. at 2×10^{-5} mmHg pressure to make the memory effect uniform until the single peak of NP_3 mentioned above was ascertained; after measurements of ammonia of high deuterium content it was passed continuously for six or more hours heating the analyzer tube. The mass spectrum of the reacted ammonia was now recorded by a self-recorder three or more times for each sample after passing it through the mass spectrometer for *ca.* 5 min. to reduce the memory effect of the analyzer tube caused by light ammonia precedingly passed, and the relative abundances of NP_3, NP_2D, NPD_2 and ND_3 were given by the relative heights of the peaks of the mass-number 17, 18, 19 and 20 ions respectively. The stability of the recordings is illustrated by repeated records in Fig. 2b. The records are not corrected for a small error of these measurements caused by the presence of the nitrogen-isotope N^{15}. The pressure of ammonia in the analyzer tube was usually constant at 6×10^{-6} mmHg during the record; the vacuum in the mass spectrometer was assured below 0.8×10^{-6} mmHg.

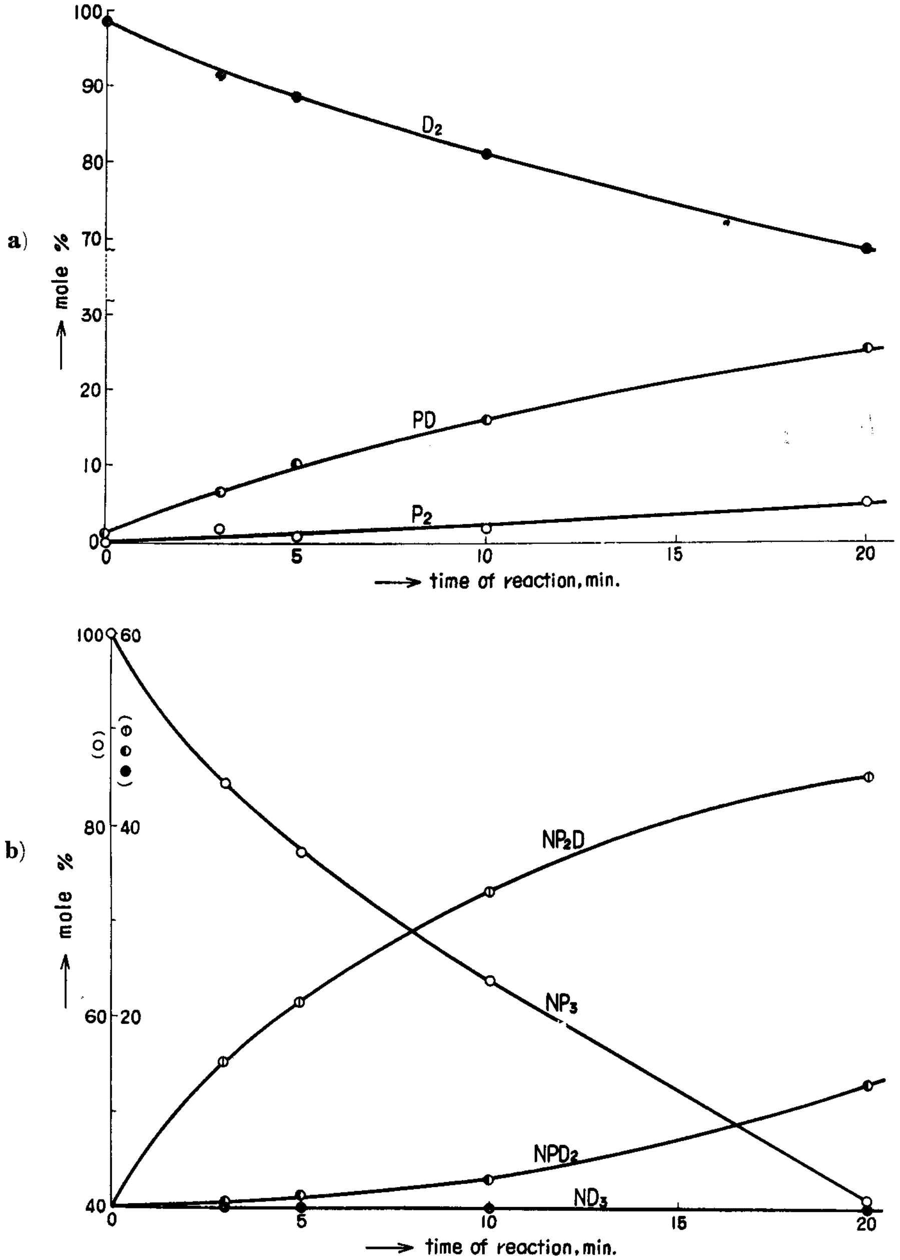


Fig. 3. Relative abundances of deutero-isomers produced by reaction of the 3:1-mixture of D_2 and NP_3 at 44 mmHg and at 100°C.
a) Hydrogen, b) Ammonia.

§ 4. Results

Fig. 3a and 3b show the changes in relative abundances of respective deutero-isomers of hydrogen and ammonia with time as observed in the first series of runs with the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg and at 100°C.

The conservations of P and D atoms in course of this reactions were satisfactorily confirmed as shown in Table 1.

TABLE 1. The conservations of P and D in course of the exchange reaction of the 3:1-mixture of D_2 and NP_3 at 44 mmHg and at 100°C.

Time, min.	3	5	10	20
D atoms transferred to ammonia, gr. atom × 10^6	8.7	11.6	18.9	34.8
P atoms transferred to hydrogen, gr. atom × 10^6	9.8	11.7	18.9	34.8

The increases in the concentration ratio [PD]/[D_2] were observed for control under the same condition (3 : 1-mixture of D_2 and NP_3 at 44 mmHg and at 100°C for 5 min.) before and after this series as mentioned in §2, being 0.114 and 0.117 respectively; the former value was chosen as the standard of the catalytic activity of the nickel film.

Fig. 4a and 4b show the results of the second series of runs with the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg and at 120°C, where the catalytic activity of the nickel film decreased during the series from 1.11 to 0.81 times the standard mentioned above.

Fig. 5a and 5b show the results of the third series of runs with the 10 : 1-mixture of D_2 and NP_3 at 110 mmHg and at 100°C, where the catalytic activity was 0.904 or 0.410 time the standard before or after this sreies.

Analysis

§ 5. Formulation of the steady formation rates of deutero-isomers at the initial stage

Scheme (1) is developed discriminating between P and D as

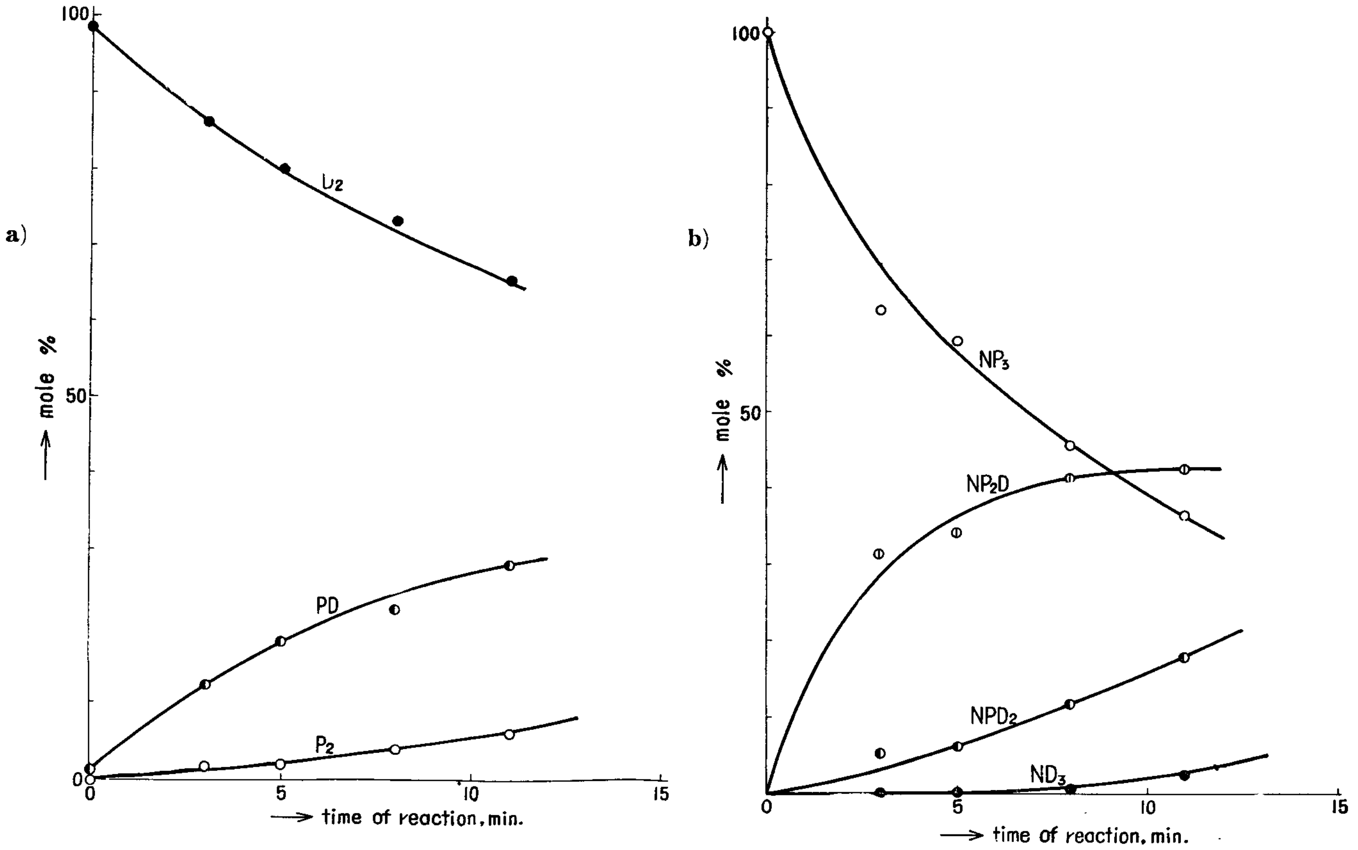


Fig. 4. Relative abundances of deutero-isomers produced by reaction of the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg and at 120°C;
a) Hydrogen, b) Ammonia.

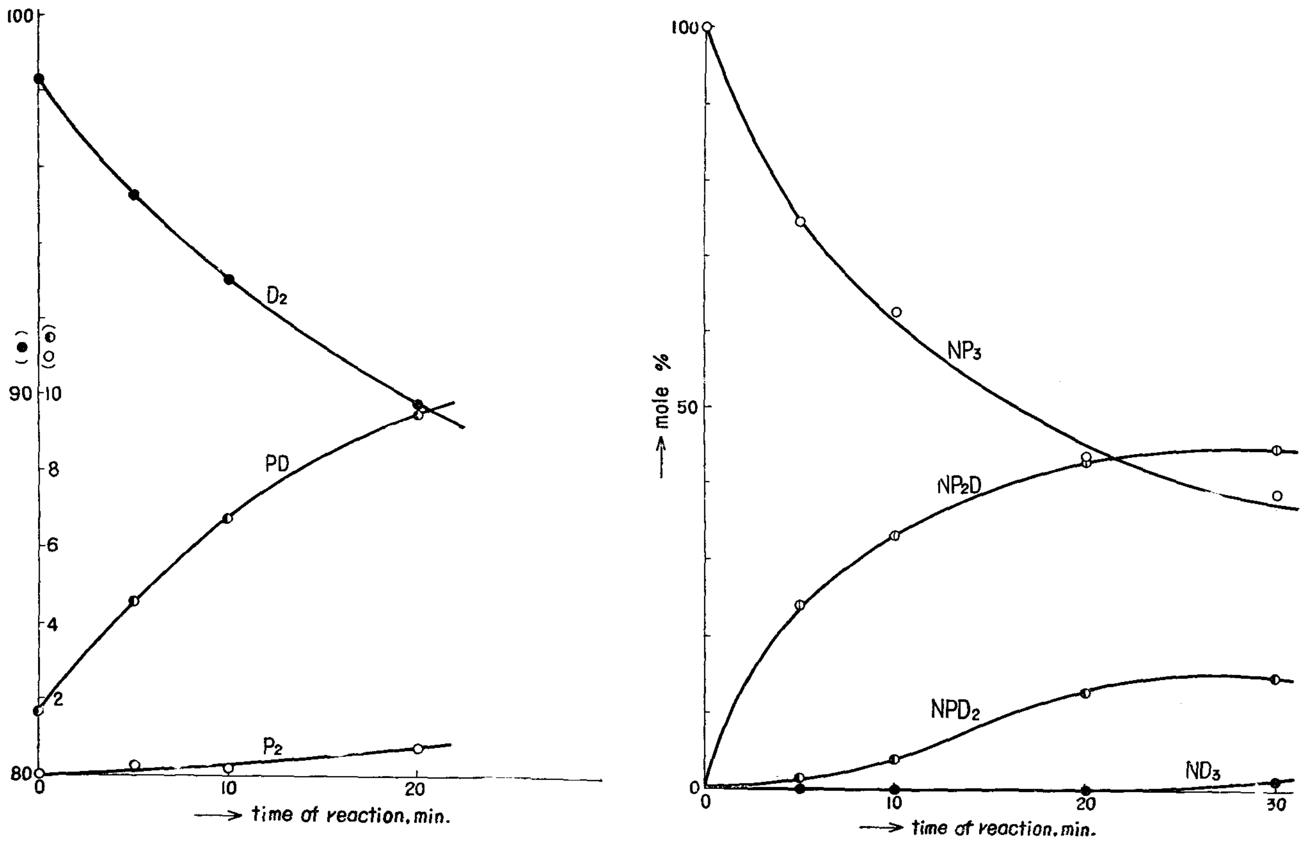
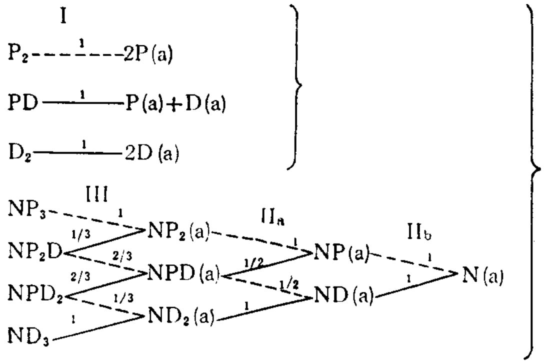


Fig. 5. Relative abundances of deutero-isomers produced by reaction of the 10 : 1-mixture of D_2 and NP_3 at 110 mmHg and at 100°C;

a) Hydrogen, b) Ammonia.



(2)

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, over the total rate of dissociation of the atom group involved, identifying the kinetic behaviour of D with that of P.

The calculation developed in the previous paper[1] of the formation rates V^{P_2}, V^{NP_3} *etc.* of P_2, NP_3 *etc.* is reproduced below. The formation rate of every atom group in Scheme (2) is given as

$$\left.\begin{aligned} V^{P_2} &= V(\mathrm{I})\{(y^{P})^2-y^{P_2}\} \\ V^{PD} &= V(\mathrm{I})(2y^{P}y^{D}-y^{PD}) \\ V^{D_2} &= V(\mathrm{I})\{(y^{D})^2-y^{D_2}\} \end{aligned}\right\}, \qquad (3.\ \mathrm{H_2})$$

$$\left.\begin{aligned} V^{NP_3} &= V(\mathrm{III})(y^{NP_2}y^{P}-y^{NP_3}) \\ V^{NP_2D} &= V(\mathrm{III})(y^{NP_2}y^{D}+y^{NPD}y^{P}-y^{NP_2D}) \\ V^{NPD_2} &= V(\mathrm{III})(y^{NPD}y^{D}+y^{ND_2}y^{P}-y^{NP_2D}) \\ V^{ND_3} &= V(\mathrm{III})(y^{ND_2}y^{D}-y^{ND_3}) \end{aligned}\right\}, \qquad (3.\ \mathrm{NH_3})$$

$$\left.\begin{aligned} V^{NP_2} &= V(\mathrm{III})\left(y^{NP_3}+\frac{1}{3}y^{NP_2D}-y^{NP_2}\right)+V(\mathrm{II_a})(y^{NP}y^{P}-y^{NP_2}) \\ V^{NPD} &= V(\mathrm{III})\left(\frac{2}{3}y^{NP_2D}+\frac{2}{3}y^{NPD_2}-y^{NPD}\right)+V(\mathrm{II_a})\left(y^{NP}y^{D}+y^{ND}y^{P}-y^{NPD}\right) \\ V^{ND_2} &= V(\mathrm{III})\left(\frac{1}{3}y^{NPD_2}+y^{ND_3}-y^{ND_2}\right)+V(\mathrm{II_a})(y^{ND}y^{D}-y^{ND_2}) \end{aligned}\right\}, \qquad (3.\ \mathrm{NH_2})$$

$$\left.\begin{aligned} V^{NP} &= V(\mathrm{II_a})\left(y^{NP_2}+\frac{1}{2}y^{NPD}-y^{NP}\right)+V(\mathrm{II_b})(y^{P}-y^{NP}) \\ V^{ND} &= V(\mathrm{II_a})\left(\frac{1}{2}y^{NPD}+y^{ND_2}-y^{ND}\right)+V(\mathrm{II_b})(y^{D}-y^{ND}) \end{aligned}\right\}, \qquad (3.\ \mathrm{NH})$$

$$V^{\mathrm{N}} = 0\,, \tag{3. N}$$

where $V(\mathrm{I})$ *etc.* denote the total forward or backward rates of steps I *etc.* balanced with each other as a whole irrespective of isotopic difference, *i.e.* at overall equilibrium, and y^{P} or y^{D} the fraction of the number of P(a) or D(a) respectively over the sum of the numbers of P(a) and D(a), $y^{\mathrm{NP_3}}$ the fraction of the number of $\mathrm{NP_3}$ over the sum of those of $\mathrm{NP_3}$, $\mathrm{NP_2D}$, $\mathrm{NPD_2}$ and $\mathrm{ND_3}$, and so on.

Specializing above equations to the intial condition $y^{\mathrm{D_2}} = y^{\mathrm{NP_3}} = 1$, $y^{\mathrm{PD}} = y^{\mathrm{P_2}} = 0$ and $y^{\mathrm{NP_2D}} = y^{\mathrm{NPD_2}} = y^{\mathrm{ND_3}} = 0$, putting rates $V^{\mathrm{NP_2}}$ *etc.* of intermediates $\mathrm{NP_2(a)}$ *etc.* individually at zero for the steady state, and noting the relation

$$y^{\mathrm{P}} + y^{\mathrm{D}} = 1\,, \tag{4}$$

we have

$$\left.\begin{aligned}
V_0^{\mathrm{P_2}} &= V(\mathrm{I})(1-y^{\mathrm{D}})^2 \\
V_0^{\mathrm{PD}} &= V(\mathrm{I})\,2y^{\mathrm{D}}(1-y^{\mathrm{D}}) \\
V_0^{\mathrm{D_2}} &= V(\mathrm{I})\,\{(y^{\mathrm{D}})^2-1\}
\end{aligned}\right\}, \tag{5. H$_2$}$$

$$\left.\begin{aligned}
V_0^{\mathrm{NP_3}} &= V(\mathrm{III})\,\{y^{\mathrm{NP_2}}(1-y^{\mathrm{D}})-1\} \\
V_0^{\mathrm{NP_2D}} &= V(\mathrm{III})\{y^{\mathrm{NP_2}}y^{\mathrm{D}} + y^{\mathrm{NPD}}(1-y^{\mathrm{D}})\} \\
V_0^{\mathrm{NPD_2}} &= V(\mathrm{III})\,\{y^{\mathrm{NPD}}y^{\mathrm{D}} + y^{\mathrm{ND_2}}(1-y^{\mathrm{D}})\} \\
V_0^{\mathrm{ND_3}} &= V(\mathrm{III})\,y^{\mathrm{ND_2}}y^{\mathrm{D}}
\end{aligned}\right\}, \tag{5. NH$_3$}$$

$$\left.\begin{aligned}
y^{\mathrm{NP_2}} &= (1-\alpha) + \alpha y^{\mathrm{NP}}(1-y^{\mathrm{D}}) \\
y^{\mathrm{NPD}} &= \alpha y^{\mathrm{NP}}y^{\mathrm{D}} + \alpha y^{\mathrm{ND}}(1-y^{\mathrm{D}}) \\
y^{\mathrm{ND_2}} &= \alpha y^{\mathrm{ND}}y^{\mathrm{D}}
\end{aligned}\right\}, \tag{5. NH$_2$}$$

$$\left.\begin{aligned}
y^{\mathrm{NP}} &= (1-\beta)\left(y^{\mathrm{NP_2}} + \frac{1}{2}y^{\mathrm{NPD}}\right) + y\,(1-y^{\mathrm{D}}) \\
y^{\mathrm{ND}} &= (1-\beta)\left(\frac{1}{2}y^{\mathrm{NPD}} + y^{\mathrm{ND_2}}\right) + \beta y^{\mathrm{D}}
\end{aligned}\right\}, \tag{5. NH}$$

where $V_0^{\mathrm{P_2}}$, $V_0^{\mathrm{NP_3}}$ *etc.* denote the initial formation rates of $\mathrm{P_2}$, $\mathrm{NP_3}$ *etc.* respectively,

$$\alpha = \frac{V(\mathrm{II_a})}{V(\mathrm{II_a}) + V(\mathrm{III})} \quad \text{and} \quad \beta = \frac{V(\mathrm{II_b})}{V(\mathrm{II_a}) + V(\mathrm{II_b})}\,. \tag{5. α), (5. β}$$

Substituting y^{NP} and y^{ND} from (5.NH) into the first and third equations of ($5.\mathrm{NH_2}$), we have

$$y^{\mathrm{NP_2}} = \frac{\alpha}{1-\alpha(1-\beta)(1-y^{\mathrm{D}})}\left\{\frac{1-\alpha}{\alpha} + \frac{1}{2}(1-\beta)(1-y^{\mathrm{D}})\,y^{\mathrm{NPD}} + \beta\,(1-y^{\mathrm{D}})^2\right\}, \tag{6. NP$_2$}$$

$$y^{\mathrm{ND}_2} = \frac{\alpha}{1-\alpha(1-\beta)y^{\mathrm{D}}}\left\{\frac{1}{2}(1-\beta)y^{\mathrm{D}}y^{\mathrm{NPD}}+\beta(y^{\mathrm{D}})^2\right\} \qquad (6.\,\mathrm{ND}_2)$$

or eliminating y^{NP}, y^{ND}, y^{NP_2} and y^{ND_2} from five equations of $(5.\mathrm{NH}_2)$ and $(5.\mathrm{NH})$,

$$y^{\mathrm{NPD}} = \frac{\dfrac{(1-\alpha)(1-\beta)y^{\mathrm{D}}}{1-\alpha(1-\beta)(1-y^{\mathrm{D}})}+\beta\gamma\left\{1-2\alpha(1-\beta)y^{\mathrm{D}}(1-y^{\mathrm{D}})\right\}}{\dfrac{2-\alpha(1-\beta)}{2}\left\{\dfrac{1}{\alpha}-(1-\beta)\alpha\right\}}, \qquad (6.\,\mathrm{NPD})$$

where

$$\gamma \equiv \frac{\alpha(1-\beta)y^{\mathrm{D}}(1-y^{\mathrm{D}})}{\{1-\alpha(1-\beta)(1-y^{\mathrm{D}})\}\{1-\alpha(1-\beta)y^{\mathrm{D}}\}}. \qquad (6.\,\gamma)$$

Eqs. $(5.\mathrm{NH}_3)$, $(6.\mathrm{NP}_2)$, $(6.\mathrm{ND}_2)$, $(6.\mathrm{NPD})$ and($6.\gamma$) give now the ratios of the initial formation rates $V_0^{\mathrm{NP}_2\mathrm{D}}$, $V_0^{\mathrm{NPD}_2}$ and $V_0^{\mathrm{ND}_3}$ to $V_0^{\mathrm{NP}_3}$ in terms of the three parameters y^{D}, α and β. The ratios of the rates $V_0^{\mathrm{P}_2}$, V_0^{PD} and $V_0^{\mathrm{D}_2}$ are determined, on the other hand, by y^{D} alone according to $(5.\mathrm{H}_2)$.

§ 6. Evaluation of parameters

The parameter y^{D} is given from the first two equations of $(5.\mathrm{H}_2)$ as

$$y^{\mathrm{D}} = V_0^{\mathrm{PD}}/(V_0^{\mathrm{PD}}+2V_0^{\mathrm{P}_2}); \qquad (7)$$

the initial values of y^{D} are calculated by the above equation as shown in Table 2 from the initial inclinations $V_0^{\mathrm{P}_2}$ and V_0^{PD} of curves P_2 and PD of the three series of experiments given respectively in Fig. 3a, 4a and 5a.

The ratios $V_0^{\mathrm{NP}_2\mathrm{D}}/V_0^{\mathrm{NP}_3}$ *etc.* of initial formation rates of deutero-ammonias $\mathrm{NP}_2\mathrm{D}$ *etc.* are similarly determined from the initial inclinations $V_0^{\mathrm{NP}_3}$ *etc.* of curves NP_3 *etc.* in Fig. 3b, 4b and 5b. These are given in Table 3 as the "obs." values of "relative rates".

It is now deduced from the experimental results as below that $\alpha \ll 1$ and $\beta \ll 1$, hence according to $(5.\alpha)$ and $(5.\beta)$ that

$$V(\mathrm{III}) \gg V(\mathrm{II}_a) \gg V(\mathrm{II}_b)\,. \qquad (8)$$

It follows from the experimental results $V_0^{\mathrm{ND}_3} \cong 0$ and the second and the last equations of $(5.\mathrm{NH}_3)$ that

$$y^{\mathrm{ND}_2} \ll 1\,, \qquad (9,\mathrm{ND}_2)$$

because $V_0^{\mathrm{NP}_2\mathrm{D}}$ is fairly large, the factor $\{y^{\mathrm{NP}_2}y^{\mathrm{D}}+y^{\mathrm{NPD}}(1-y^{\mathrm{D}})\}$ of the second equation of $(5.\mathrm{NH}_3)$ is less than unity and $y^{\mathrm{D}}>0.7$ as given in Table 2. We have from $(9.\mathrm{ND}_2)$ and the last equation of $(5.\mathrm{NH}_2)$ that either or both of α and y^{ND} are extremely small compared with unity.

Let $\quad y^{\mathrm{ND}} \ll 1\,. \qquad (9,\mathrm{ND})$

It follows from the second equation of (5. NH_2)

$$y^{\mathrm{NPD}} \cong \alpha y^{\mathrm{D}} \,. \qquad \text{(9. NPD)}$$

We have now from the last equation of (5. NH), (9. ND_2) and (9. NPD)

$$y^{\mathrm{ND}} = \left\{ \frac{\alpha}{2} + \beta\left(1 - \frac{\alpha}{2}\right) \right\} y^{\mathrm{D}} \,,$$

which states, according to (9. ND), that the terms in the parentheses should be individually extremely small compared with unity, *i. e.*

$$\alpha \ll 1 \quad \text{and} \quad \beta \ll 1 \,. \qquad (9.\,\alpha),\ (9.\,\beta)$$

Suppose now y^{ND} is not vanishingly smaller than unity. It follows that α must be vanishingly smaller than unity according to (9. ND_2) and the last equation of (5. NH_2), hence that $y^{\mathrm{NPD}} \ll 1$ by the second equation of (5. NH_2). We have from the latter inequality, (9. ND_2) and the third equation of (5. NH_3) that $V_0^{\mathrm{NPD}_2}$ is as vanishingly small as $V_0^{\mathrm{ND}_3}$. Since this is not the case, y^{ND} must be so small or (9. α) and (9. β) should hold, hence we have (8) according to (5. α) and (5. β).

The present analysis was carried out for the first approximation neglecting $V(\mathrm{II_b})$ but taking $V(\mathrm{II_a})$ into account. Neglecting thus β, we have from (6. NP_2), (6. $ND)_2$, (6. NPD) and (6. γ)

$$\left. \begin{aligned} y^{\mathrm{NP}_2} &= \frac{\alpha}{1-\alpha(1-y^{\mathrm{D}})} \left\{ \frac{1-\alpha}{\alpha} + \frac{1}{2}(1-y^{\mathrm{D}})\, y^{\mathrm{NPD}} \right\} \\ y^{\mathrm{NPD}} &= \frac{2\alpha}{2-\alpha}\, y^{\mathrm{D}} \\ y^{\mathrm{ND}_2} &= \frac{\alpha}{2(1-\alpha y^{\mathrm{D}})}\, y^{\mathrm{D}} y^{\mathrm{NPD}} \end{aligned} \right\} . \qquad (10.\,\mathrm{NH_2})$$

TABLE 2. The initial formation rates of PD and P_2 observed and the values of y^{D} calculated according to Eq. (7)

No. of series	Condition of reaction			Initial formation rate, H_2-mole %/min			y^{D}
	Mixing ratio, $[D_2]/[NP_3]$	Pressure, mmHg	Temp. °C	$V_0^{D_2}$	V_0^{PD}	$V_0^{P_2}$	
1	3	44	100	− 2.30	1.90	0.40	0.70
2	3	44	120	− 4.78	4.10	0.68	0.75
3	10	110	100	− 0.65	0.63	0.02	0.94

The ratios $V_0^{\mathrm{NP_2D}}/V_0^{\mathrm{NP_3}}$ and $V_0^{\mathrm{NPD_2}}/V_0^{\mathrm{NP_3}}$ depend respectively on the value of the parameter α, besides on that of y^{D} already evaluated, according to Eqs. (5. NH_3) and (10. NH_2). The value of α is, hence, calculated conversely from the observed values of $V_0^{\mathrm{NP_2D}}/V_0^{\mathrm{NP_3}}$ or $V^{\mathrm{NPD_2}}/V_0^{\mathrm{NP_3}}$ and y^{D}. Table 3 shows the value α_1 of α thus calculated from $V_0^{\mathrm{NP_2D}}/V_0^{\mathrm{NP_3}}$ and that α_2 from $V_0^{\mathrm{NPD_2}}/V_0^{\mathrm{NP_3}}$;

TABLE 3. Calculated relative

No. of series	Condition of reaction	Catalytic activity	$V_0^{NP_3}$ mole %/min.	y^D	Relative	
					Remark	$-\frac{V_0^{NP_2D}}{V_0^{NP_3}}$
1	$[D_2]/[NP^{\varepsilon}]=3$, 44 mmHg, 100°C	1.000	$-$ 6.80	0.704	obs.	98.0
					calc.	98.0
2	$[D_2]/[NP_3]=3$, 44 mmHg, 120°C	1.11	$-$ 18.9	0.751	obs.	88.5
					calc.	88.4
3	$[D_2]/[NP_3]=10$, 110 mmHg, 100°C	0.904	$-$ 7.2	0.940	obs.	97.0
					calc.	97.0

α_{av} is the average of α_1 and α_2. Close coincidence of α_1 and α_2 confirms the consistency of the present analysis.

The values of $V_0^{NP_2D}/V_0^{NP_3}$ and $V_0^{NPD_2}/V_0^{NP_3}$ are now calculated on the basis of α_{av} according to (5. NH_3) and (10. NH_2) as shown by "calc." values in the Table; the value of $V_0^{ND_3}/V_0^{NP_3}$ is similarly calculated as shown there on the same base according to (5. NH_3) and (10. NH_2).

The values of $V(II_a)/V(III)$ in the third last column of Table 3 were calculated on the base of α_{av} according to (5. α). The value of $V(I)/V(III)$ in the second last column of the Table were calculated by the equation

$$\frac{V(I)}{V(III)}=\frac{\alpha y^D}{2(1-\alpha)(1-y^D)}\left(\frac{1}{\alpha}-\frac{\alpha}{2-\alpha}\right)$$

which was derived by eliminating four quantities, y^{NPD}, y^{ND_2}, y^P and $V(II_a)/V(III)$ from five equations, *i.e.* the steady state equation for D(a) at the initial stage of the reaction

$$y^D\left\{2V(I)+V(II_a)+V(III)\right\}=2V(I)+V(II_a)\left(\frac{1}{2}y^{NPD}+y^{ND_2}\right),$$

(4), (5. α) and the last two equations of (10. NH_2).

The values of $-V_0^{NP_3}/V(III)$ in the last column of the Table were calculated from the values of α_{av} and y^D by the first two equations of (10. NH_2) and the first one of (5. NH_3).

We now determine the activation energies of steps I, II_a and III of Scheme (1) respectively from the results given in Table 3 of series 1 and 2.

We have from the values of $V(II_a)/V(III)$ respectively of series 1 and 2 given in Table 3 that

$$E(II_a)-E(III)=-R\frac{d\ln\{V(II_a)/V(III)\}}{d(1/T)}=26.5\text{ kcal.},\tag{11}$$

formation rates of deuteroammonias

rates, %		α			$\frac{V(\mathrm{II_a})}{V(\mathrm{III})}$	$\frac{V(\mathrm{I})}{V(\mathrm{III})}$	$\frac{V_0^{\mathrm{NP_3}}}{V(\mathrm{III})}$
$-\frac{V_0^{\mathrm{NPD_2}}}{V_0^{\mathrm{NP_3}}}$	$-\frac{V_0^{\mathrm{ND_3}}}{V_0^{\mathrm{NP_3}}}$	α_1	α_2	α_{av}			
2.0	0.0	0.029	0.029	0.029	0.03	1.22	0.71
2.0	0.0						
11.0	0.5	0.154	0.155	0.1545	0.18	1.57	0.86
10.8	0.8						
3.0	0.0	0.0425	0.0435	0.0430	0.05	8.16	0.94
2.9	0.1						

and similarly from the values of $V(\mathrm{I})/V(\mathrm{III})$ or $V_0^{\mathrm{NP_3}}/V(\mathrm{III})$ of the series 1 and 2,

$$E(\mathrm{I})-E(\mathrm{III}) = -R\frac{d\ln\{V(\mathrm{I})/V(\mathrm{III})\}}{d(1/T)} = 3.7\ \mathrm{kcal.} \tag{12}$$

or

$$E^{\mathrm{NP_3}}-E(\mathrm{III}) = -R\frac{d\ln\{-V_0^{\mathrm{NP_3}}/V(\mathrm{III})\}}{d(1/T)} = 2.8\ \mathrm{kcal.}, \tag{13}$$

where

$$E^{\mathrm{NP_3}} = -R\frac{d\ln(-V_0^{\mathrm{NP_3}})}{d(1/T)}\,.$$

The activation energy $E^{\mathrm{NP_3}}$ is now determined from $V_0^{\mathrm{NP_3}}$ of series 1, *i.e.* -6.80 mole %/min., and the value of $V_0^{\mathrm{NP_3}}$ of series 2 redeced to the standard catalytic activity, *i.e.* $-18.9/1.11 = -17.03$ mole %/min. as

$$E^{\mathrm{NP_3}} = 13.4\ \mathrm{kcal.} \tag{14. NP$_3$}$$

We have from (11), (12), (13) and (14. NP_3)

$$E(\mathrm{III}) = 10.6\ \mathrm{kcal.}, \tag{14. III}$$

$$E(\mathrm{II_a}) = 37.1\ \mathrm{kcal.}, \tag{14. II$_a$}$$

$$E(\mathrm{I}) = 14.3\ \mathrm{kcal.} \tag{14. I}$$

Fig. 6 shows logarithms of $V(\mathrm{I})$, $V(\mathrm{II_a})$ and $V(\mathrm{III})$ plotted against the reciprocal of absolute temperature by straight lines denoted respectively by I, $\mathrm{II_a}$ and III on the base of their relative magnitudes determined from series 1 as given in Table 3 and their inclinations in terms of the activation energies given above. Fig. 6 illustrated the so-called "structure" of the present exchange reaction of the 3 : 1-mixture of D_2 and NP_3 at 44 mmHg total pressure or the

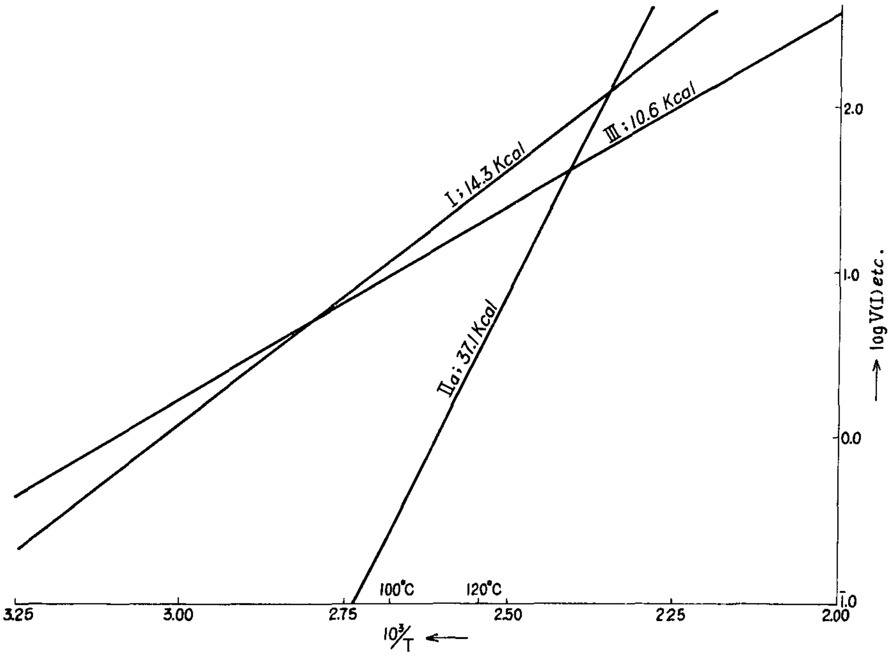


Fig. 6. The structure of the reaction of the 3 :1-mixture of D_2 and NP_3 at 44 mmHg and at temperatures in the neighbourhood of 100°C.

relative magnitudes of the rates of steps I, II_a and III in the neighbourhood of 100°C.

§ 7. Remarks on the results

1. The structure of the catalytic exchange between D_2 and NP_3 was determined in the preceding paragraphs from the formation rates of deutero-isomers of ammonia as well as of hydrogen evaluated by the total analysis of the reaction products.

2. The step $NH(a) \rightarrow N(a) + H(a)$ was concluded in §6 to be extremely slow compared with the other steps of Scheme (1). This is in conformity with the conclusions arrived at independently in this laboratory; Horiuti *et. al.* have determined the stoichiometric number of the rate-determining step as 2 for the ammonia synthesis reaction catalyzed by ammonia synthetic iron catalyst[5][6] which confines the possible rate-determining step to one of the three steps, III, II_a or II_b of Scheme (1), and concluded frcm the analysis of the decomposition rate of ammonia in the presence of hydrogen that the rate-determining step is II_b[6]. Azuma[7] has recently concluded on the basis of the field-emmision micro-

scopic observations of hydrogen, nitrogen or ammonia adsorbed on tungsten tip that step II$_b$ is the slowest one among those of Scheme (1') and $N_2 \rightarrow 2N(a)$, *i.e.* the chemisorption of nitrogen.

3. It is concluded from the structure in Fig. 6 that the rate of catalyzed exchange between hydrogen and ammonia should be controlled at room temperature by step I, which is slower than III. This conclusion is in concordance with that arrived at by HORIUTI and SUZUKI[8], that the chemisorption of hydrogen, *i.e.* I in this case, is the rate-determining step of the catalyzed exchange between P_2 and ND_3 in the presence of annealed nickel wire at 31°C.

4. The value of $V(\mathrm{I})/V(\mathrm{III})$ increases, while that of $V(\mathrm{II_a})/V(\mathrm{III})$ remains almost constant with increase of hydrogen partial pressure as revealed from the comparison of the results of series 1 and 3 in Table 3. Further experiments would by necessary, however, to draw any quantitative conclusion on the kinetics of the exchange reaction.

Appendix

The result of Fig. 7 is obtained with 99.5 D% deuterium gas from cylinder, ionizing electrons in the mass spectrometer being accelerated at 33 V; i_2 i_3 or

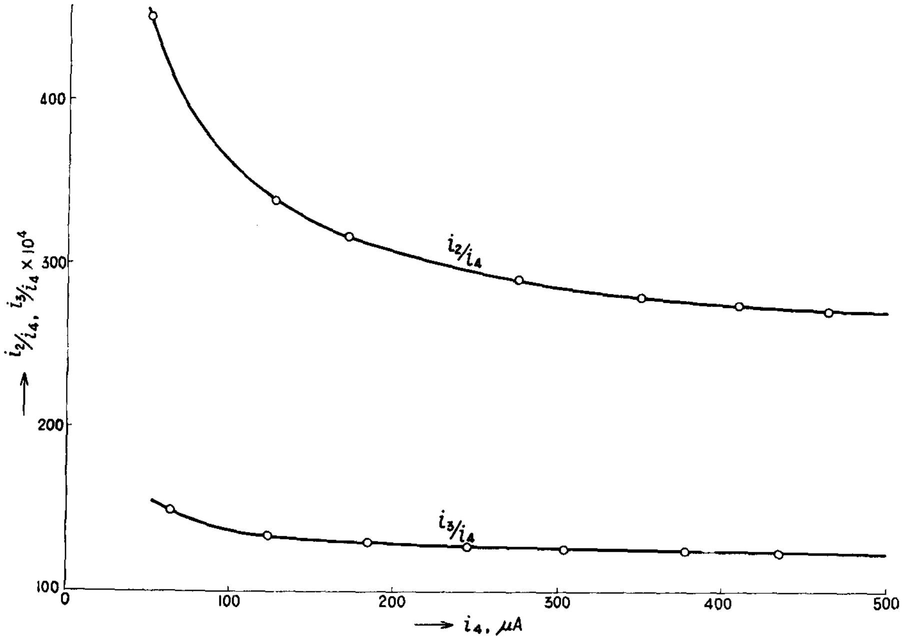


Fig. 7. Relations between ratio of ion-currents i_2/i_4 or i_3/i_4 and i_4 with 99.5 D% deuterium gas.

i_4 is the ion-current of mass-number 2, 3 or 4 ion respectively.

The ratio i_3/i_4 is almost constant along with the change of i_4 except in the region of small values of i_4, where the memory of the analyzer tube of the mass spectrometer may be effective, hence the value of i_3/i_4 at i_4 larger than 300 μA is accepted as the concentration ratio [PD]/[D_2] in D_2 gas or reacted hydrogen*).

The ratio i_2/i_4 in the case of 99.5 D% deuterium varies, on the other hand, markedly with increase of i_4 as shown in Fig. 7. The current i_2 should be solely due to ions D^+ produced from practically pure D_2 in this case, hence the observed variation of i_2/i_4 shows that the abundance of D^+ sensibly depends upon the pressure of the gas in the ionization chamber. This ratio varies, besides, with change of the voltage V_e applied to ionizing electrons as shown

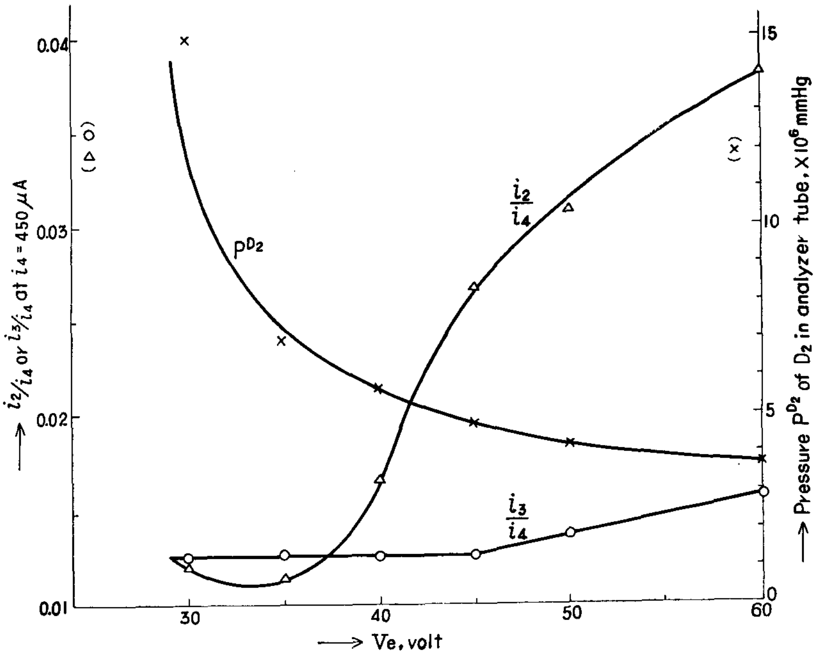


Fig. 8. Dependency of ion-current ratio i_2/i_4 or i_3/i_4 and the pressure of the sample upon the electron-accelerating voltage in the case of deuterium gas of 99.5 D%.
Ion accelerating voltage: 845 v.
Total emmision current: 450 μA.
Trapped current: 10 μA.

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*) The gain of the amplifier for the ion-current i_2 and i_3 was almost equal to that for i_4, so that i_3/i_4 may be taken to give [PD]/[D_2] directly.

in Fig. 8, whereas the pressure of gas in the ionization chamber for $i_4 = 450\ \mu A$ increases rapidly as the voltage V_e decreased below *ca.* 30 V. With regard to these circumstances V_e was fixed at 33 V for the present measurement and the concentration ratio $[P_2/[D_2]$ of P_2 to D_2 in reacted hydrogen was given as the excess of its values of i_2/i_4 over that $(i_2/i_4)_0$ of the unreacted D_2 gas, *i.e.*

$$[P_2]/[D_2] = i_2/i_4 - (i_2/i_4)_0$$

at the same value of i_4. This procedure may be allowable for the determination of $[P_2]/[D_2]$ at the initial stage of the present reaction, where deuterium is abundant enough to form D^+ practically the same as in the cases of unreacted deuterium gas.

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