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ON THE SORPTION OF NITROGEN ON COMMERCIAL AMMONIA SYNTHESIS CATALYST

By

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Introduction

The sorption of nitrogen on commercial ammonia synthesis catalyst or pure iron powder has been observed by EMMETT and BRUNAUER¹⁾ at 760 mmHg and by KWAN²⁾ at low pressures below several mmHg. On the basis of the results the former two authors have suggested and recently TRAPNELL³⁾ as well that nitrogen is adsorbed on the surface of the catalyst dissociated into atoms, while KWAN proposed an empirical rate formula of power type.

Present authors have found, analysing the experimental results of EMMETT and BRUNAUER, of KWAN and supplementary ones of the present authors, that they can not be accounted for by a simple picture of dissociative adsorption but by the mechanism of the latter accompanied by subsequent absorption of adsorbed nitrogen atoms into the interior of the catalyst and that the results of the analysis lead to conclusions in concordance with other knowledges of the catalyst and the synthesis reaction.

Below will be described the supplementary experiments, the analysis of the experimental data and the inferences concordantly drawn from the analysed results.

§ 1. Experimental

The supplementary experiments have been conducted at 300°C and low initial pressures according to the method of KWAN²⁾ ⁴⁾ i. e. the

*¹⁾ Research Institute for Catalysis, Hokkaido University.

1) P. H. EMMETT and S. BRUNAUER, J. Am. Chem. Soc. **56**, 35 (1934).

2) T. KWAN, This Journal **3**, 16 (1953).

3) B. M. W. TRAPNELL, "Chemisorption", p. 184, London, 1955.

4) T. KWAN, This Journal **1**, 81 (1949).

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TABLE 1. Pressure of Nitrogen under Sorption, mmHg

Sorbent: doubly promoted ammonia synthesis catalyst, 10.4 gm

Gas volume: 430 cc

Temp. Time (min.)	Runs	300°C			400°C				450°C		
		1	2	3	1K ¹⁾	2K ¹⁾	3K ¹⁾	4K ¹⁾	5K ^{*)}	6K ^{*)}	7K ^{*)}
0		1.59	0.749	0.306	1.91	1.84	0.619	0.225	2.41	0.728	0.275
1		1.37	.631	.262	1.33	1.33	.360	.130	1.62	.333	.121
2		1.345	.612	.252	1.18	1.20	.270	.0850	1.40	.225	.060
3		1.31	.592	.237	1.08	1.08	.222	.0575	1.245	.159	.030
4		1.29	.576	.223	0.98	1.00	.180	.0395	1.14	.1125	.014
5		1.26	.561	.218	.92	0.935	.145	.0271	1.045	.082	.0082
6		1.24	—	.210	.85	.860	.123	.0187	1.00	.062	.00415
7		—	.529	.203	.82	.824	.104	.0126	0.920	.0463	—
8		1.20	—	.199	.78	.780	.090	.0080	.855	.0340	—
9		—	.514	.194	—	.745	.076	.0067	.820	.0255	—
10		1.175	—	.184	.72	.725	.064	.0038	.790	.0200	—
11		—	.491	—	—	—	—	—	—	—	—
12		1.15	—	.175	—	.625	.045	—	.735	.0123	—
12.1		—	—	—	.68	—	—	—	—	—	—
13		—	.481	—	—	—	—	—	—	—	—
14		1.13	—	.167	.63	—	.033	—	.695	.0080	—
15		—	.466	—	—	—	—	—	—	—	—
15.3		—	—	—	—	.600	—	—	—	—	—
16		1.11	—	.165	.60	.590	.0234	—	.660	.0060	—
18		1.095	.442	.155	.555	.565	.0164	—	.625	.00515	—
20		1.08	—	.148	.53	.530	.012	—	.605	—	—
21		—	.430	—	.51	—	—	—	—	—	—
22		—	—	—	—	.500	.0081	—	—	—	—
23		1.06	—	—	.475	—	—	—	—	—	—
24		—	.418	—	—	.485	—	—	.560	—	—
25		—	—	.136	.460	—	—	—	—	—	—
26		—	—	—	—	.460	—	—	—	—	—
27		1.04	—	—	.44	.435	—	—	—	—	—
28		—	.404	.121	.42	—	—	—	.525	—	—
30		1.02	—	—	.40	—	—	—	—	—	—
32		—	—	—	—	—	—	—	.480	—	—
33		—	.389	—	.39	—	—	—	—	—	—
34		—	—	—	—	—	—	—	—	—	—
35		0.993	—	—	.37	.385	—	—	—	—	—
36		—	—	—	.344	—	—	—	.455	—	—
39		—	.364	—	—	—	—	—	—	—	—
40		.975	—	—	—	.345	—	—	—	—	—
42.5		—	—	—	.305	.335	—	—	—	—	—
45		.945	.345	—	.28	.305	—	—	—	—	—
50		.915	.335	—	.265	—	—	—	—	—	—
55		.880	—	—	—	—	—	—	—	—	—
60		.870	—	—	—	—	—	—	—	—	—

*) Unpublished result of KWAN.

pressure decrease was observed in a space of constant, 430 cc volume in the presence of the doubly promoted catalyst employed by KWAN which was of 10.4 gm weight before reduction. After every series of the sorption experiment, a quantity of hydrogen gas was circulated as did by KWAN over the catalyst kept at 550°C through a liquid trap, until no consumption of hydrogen was observed by a manometer. A few series of observation have also been conducted at 450°C for a check of the activity of the catalyst. Our result reproduced KWAN's result at 300°C and 1.57 mmHg initial pressure quantitatively, whereas that at 450°C and 0.728 mmHg initial pressure not quite.

The surface area of the reduced catalyst was 13.0 m² per gm of the catalyst as determined by BET method using nitrogen as adsorbate at the b. p. of liquid nitrogen.

Table 1 shows the results of the present authors at 300°C side by side with those of KWAN, signified by K which are subject to the present analysis.

§ 2. Simple dissociative adsorption

The rate \dot{S} of sorption of nitrogen on the catalyst is expressed as

$$\dot{S} = \bar{k}_1 AP(1-\theta)^2 - \bar{k}_2 A\theta^2, \quad (1)$$

neglecting interaction between adsorbed nitrogen atoms, where \bar{k}_1 and \bar{k}_2 are rate constants, A the surface area of the catalyst, P the pressure of nitrogen and θ the covered fraction of surface. The θ is proportional, according to the present picture, to the sorbed amount, S i. e.,

$$\theta = \frac{1}{N} \cdot S, \quad (2)$$

where N is the proportionality constant or the amount of nitrogen adsorbed at $\theta=1$.

We have from (1) and (2)

$$\left\{ \frac{S^2 \bar{k}_1 A / N^2 + \dot{S}}{P} \right\}^{\frac{1}{2}} = (\bar{k}_1 A)^{\frac{1}{2}} - \left(\frac{\bar{k}_2 A}{N^2} \right)^{\frac{1}{2}} \cdot S, \quad (3)$$

which states that its left side varies linearly with S . The S is now proportional to the pressure decrease $P_0 - P$ i. e. to the difference of the initial pressure P_0 and the momentary pressure P in the present experimental procedure described in §1, whereas to the volume de-

crease which was followed by EMMETT and BRUNAUER¹⁾ at constant pressure.

It was found that the linear relation of (3) was satisfied neither by the results of experiments of Table 1 nor by those of EMMETT and BRUNAUER¹⁾ at all.

The above picture was then discarded and the absorption of nitrogen atoms into the interior of the catalyst was taken into account as detailed in the next section.

§ 3. Consecutive adsorption and absorption

Our picture of sorption is now that nitrogen molecule is adsorbed on the surface to form adsorbed atoms N(a) statistically independent of each other, which are subsequently absorbed to result in dissolved atoms N(s) in the interior of the catalyst i. e. as



The rate \dot{S} of sorption is also expressed, provided that the forward rate of absorption is proportional to $A\theta$ and the backward rate is proportional to the amount $A(1-\theta)$ of bare sites of adsorption and to the concentration $\frac{S-N\theta}{V}$ of dissolved atoms N(s) i. e. overall sorbed quantity S minus adsorbed quantity $N\theta$ over the volume V of the catalyst, as

$$\dot{S} = N\dot{\theta} + \bar{k}_2 A\theta - \bar{k}_2 \frac{A}{V} (S - N\theta)(1 - \theta), \quad (5)$$

where \bar{k}_2 or \tilde{k}_2 is the respective rate constant.

Eq. (5) gives by integration

$$S = N\theta + \bar{k}_2 A \int_0^\theta \theta dt - \bar{k}_2 \frac{A}{V} \int_0^\theta (S - N\theta)(1 - \theta) dt,$$

or

$$Y = \frac{1}{\bar{k}_2 A} + \frac{\tilde{k}_2}{\bar{k}_2 V} X, \quad (6. L)$$

where

$$Y = \frac{\int_0^\theta \theta dt}{S - N\theta}, \quad X = \frac{\int_0^\theta (S - N\theta)(1 - \theta) dt}{S - N\theta}. \quad (6. Y), (6. X),$$

The θ in the expression is expressed according to (1), which remains

valid even in this case, as

$$\theta = \frac{\bar{k}_1 P - \sqrt{\bar{k}_1 P \bar{k}_1 - (\bar{k}_1 P - \bar{k}_1) S/A}}{\bar{k}_1 P - \bar{k}_1} \quad (*) \quad (7)$$

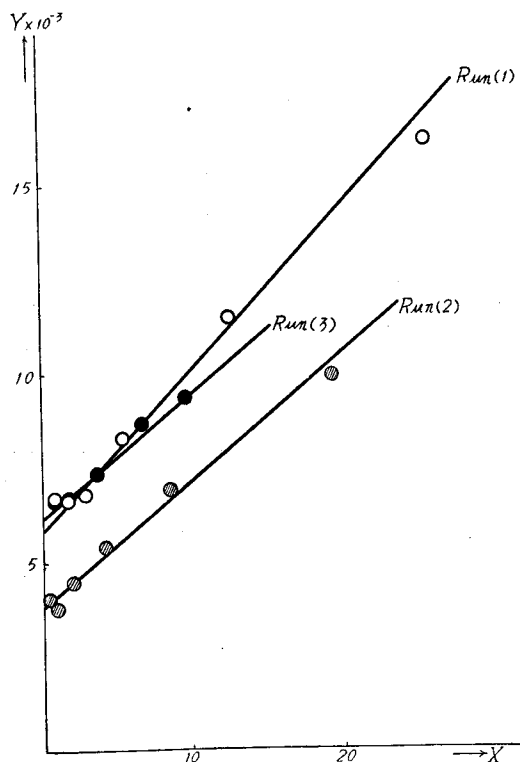


Fig. 1 Linear relation between

$$Y = \frac{\int_0^t \theta dt}{S - N\theta} \quad \text{and} \quad X = \frac{\int_0^t (S - N\theta)(1 - \theta) dt}{S - N\theta}$$

at 300°C

Run (1); $P_0 = 1.59$ mmHg

Run (2); $P_0 = 0.749$ mmHg

Run (3); $P_0 = 0.306$ mmHg

$\bar{k}_1 = 1.68 \times 10^{-12}$ mol min⁻¹ mmHg⁻¹ cm⁻²

$N = 1.2 \times 10^{-3}$ mol (10¹⁵ sites cm⁻²)

within ± 10 percent, whereas practically N and \bar{k}_1 , not individually but a functional relation between them instead over a considerable

Eq. (6. L) shows the linear relation between Y and X which has now been thrown to the experimental test; Y and X are worked out according to (6. Y), (6. X), and (7) from the observed values of S, P, \dot{S} and a trial set of values of \bar{k}_1 and N .

Fig. 1 shows the linear relation for runs 1, 2 and 3, Table 1. The inconformities of the straight lines show, according to (6. L), discrepancies between constants \bar{k}_2 's and \bar{k}_2 's appropriate to respective runs. The linear relation fits in with KWAN's runs with fluctuations in \bar{k}_2 or \bar{k}_2 of the same extent. Fig. 2 shows the linear relation fitted to runs 3 and 10 of EMMETT and BRUNAUER's observation conducted at 449°C and 397°C and at constant, 1 atm pressure with the same value of \bar{k}_1 determined from runs of present authors and KWAN conducted at low pressures.

The linearity (6. L) fixes \bar{k}_1 , within ± 10 percent, whereas practically N and \bar{k}_1 , not individually but a functional relation between them instead over a considerable

*) Plus sign of the root excludes the region of θ between 0 and 1, which is physically significant.

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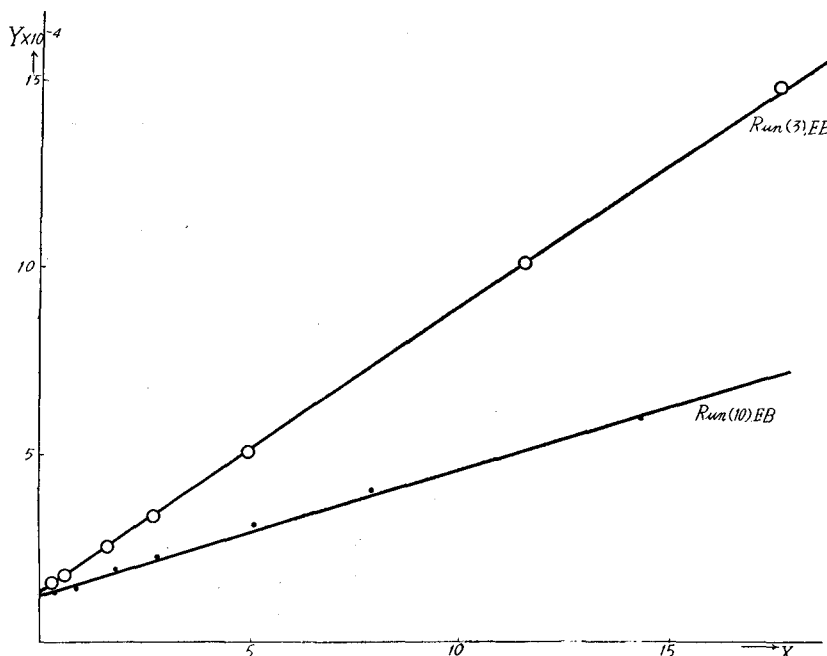


Fig. 2 Linear relation between $Y = \frac{\int_0^t \theta dt}{S - N\theta}$ and $X = \frac{\int_0^t (S - N\theta)(1 - \theta) dt}{S - N\theta}$ fitted to the observation of EMMETT and BRUNAUER at 1. atm N_2 -pressure

Run (3), EB; 449°C, $\bar{k}_1 = 1.5 \times 10^{-11}$ mol min⁻¹ mmHg⁻¹ cm⁻² }
 Run (10), EB; 397°C, $\bar{k}_1 = 9.2 \times 10^{-12}$ mol min⁻¹ mmHg⁻¹ cm⁻² }
 $N = 3.26 \times 10^{-4}$ mols (10^{15} sites cm⁻²)

range of variation of the respective quantities. Prescribing N -value at that corresponding to 10^{15} sites for adsorption per cm², \bar{k}_1 -values for respective series are individually fixed, which fluctuate at the same temperature within a factor of 2. The \bar{k}_2 varies with N too, leaving the linear relation valid, but not so much as \bar{k}_1 does and \bar{k}_2 still less as shown in Table 2.

Table 3 gives the values of \bar{k}_1 at different temperatures worked out from the observed data given in Table 1.

Inferences are drawn in subsequent sections from the values of rate constants thus determined.

TABLE 2. Variation of Rate Constants with N -Value, Calculated from 1 K, Table 1

Run Rate const. N (mol)	1 K		
	\tilde{k}_1 mol min ⁻¹ cm ⁻²	\tilde{k}_2 mol min ⁻¹ cm ⁻²	\tilde{k}_2 min ⁻¹ cm ⁻²
1.2×10^{-2}	7×10^{-6}	1.8×10^{-9}	5.3×10^{-10}
1.0×10^{-3} *)	6.5×10^{-8}	1.8×10^{-10}	1.2×10^{-12}
1.2×10^{-4}	5×10^{-10}	1.7×10^{-11}	5.1×10^{-12}

TABLE 3 \tilde{k}_1 -Values

Temp. °C	300	400	450
Runs	1. 2. 3.	1K, 2K, 3K, 4K	5K, 6K, 7K
\tilde{k}_1 mol min ⁻¹ mmHg ⁻¹ cm ⁻²	$1.6 \sim 1.9 \times 10^{-12}$	$0.84 \sim 1.1 \times 10^{-11}$	$1.4 \sim 1.7 \times 10^{-11}$

§ 4. Number of sites of adsorption

The forward rate \bar{v}_1 of adsorption per unit area on a bare surface is now

$$\bar{v}_1 = N_A \tilde{k}_1 P \quad (8)$$

where N_A is AVOGRADRO'S number.

The same quantity is expressed, according to the generalized theory of reaction rate⁵⁾, assuming transmission coefficient κ unity, as

$$\bar{v}_1 = \frac{kT}{h} G_1 \frac{q^*}{Q^{N_2}} N^{N_2} \text{ **),} \quad (9)$$

where G_1 is the number of sites of adsorption for the activated complex per unit area, q^* the BOLTZMAN factor of the reversible work $\epsilon^{**})$ required to bring up the activated complex from its standard state onto the evacuated site of adsorption, N^{N_2} the number of nitrogen molecule per unit volume and Q^{N_2} the partition function of a single nitrogen molecule in unit volume. Q^{N_2} is expressed with a good approximation as

5) J. HORIUTI, This Journal 1, 8 (1948).

*) This value of N corresponds to 10^{15} sites of adsorption per cm².

***) Cf. Ref. 5), Eq. (24. 9 \bar{v}); The probability θ_{σ^*} , that the site σ^* of adsorption for the activated complex is accessible to the latter is put unity for the bare surface.

*) Cf. Ref. 5), §7.

$$Q^{N_2} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{4\pi^2 I kT}{h^2} \exp\left(-\frac{\epsilon^{N_2}}{kT}\right), \quad (10)$$

where m is the mass of the molecule, I the moment of inertia and ϵ^{N_2} the energy of the ground state.

We have from (8) and (9)

$$\bar{k}_1 = \frac{c}{h} \cdot \frac{G_1}{N_A} \cdot \frac{q^*}{Q^{N_2}}, \quad (11)$$

where

$$c = \frac{kT N^{N_2}}{P} = 1.36 \times 980$$

is the conversion factor of the pressure unit from mmHg to dyne per cm^2 .

Activation energy $RT^2 \frac{d \log \bar{k}_1}{dT}$ of the adsorption is now

$$RT^2 \frac{d \log \bar{k}_1}{dT} = \epsilon^* - \epsilon^{N_2} - \frac{5}{2} RT, \quad (12)$$

assuming that ϵ^* is constant independent of temperature, which is exactly valid for sufficiently large vibrational frequencies of the activated complex. We have on the other hand from the \bar{k}_1 -values in Table 3 $RT^2 \frac{d \log \bar{k}_1}{dT} = 10 \pm 2$ Kcal/mol and hence, taking T there that of 400°C ,

$$\epsilon^* - \epsilon^{N_2} = 6.6 \pm 2 \text{ Kcal}, \quad (13)$$

or

$$G_1 = 0.4 \sim 8.0 \times 10^{14}, \quad (14)$$

from (10), (11), (13) and the values of constants

$$\bar{k}_1 = 9.0 \times 10^{-12} \text{ at } 400^\circ\text{C}, \quad m = 4.65 \times 10^{-23}, \quad I = 1.38 \times 10^{-39} \text{ cm}^2. \quad (15)$$

Eq. (14) gives the correct order of magnitude of G_1 in confirmation of the premise of the present analysis.

§ 5. Rate-determining step of catalysed ammonia synthesis

A number of authors⁶⁾ have suggested that the rate of catalysed

*) LANDOLT-BÖRENSTEIN, "Tabellen", Eg. IIIc, p. 2352.

6) M. TEMKIN and W. PYZHEV, Acta Physicochim. 17, 323 (1940).

K. S. LOVE and P. H. EMMETT, J. Am. Chem. Soc., 63, 3297 (1941).

S. BRUNAUER, K. S. LOVE and R. G. KEENAN, J. Am. Chem. Soc. 64, 751 (1942).

P. ZWIETERING and J. J. ROUKENS, Trans. Faraday Soc. 50, 178 (1954).

ammonia synthesis in the presence of commercial catalyst is governed by the dissociative adsorption of nitrogen. ENOMOTO and HORIUTI⁷⁾ have found, however, 2 for the value of stoichiometric number⁸⁾ $\nu(r)$ of the rate-determining step of the reaction,



in the presence of the same catalyst as of the present use.

In the above investigation of ENOMOTO and HORIUTI⁷⁾, the 1:3 nitrogen-hydrogen mixture was kept in equilibrium at 404 mmHg total pressure with ammonia of 0.74, 0.46 or 0.39 mmHg partial pressure respectively at 400°C, 430°C or 450°C. The latter authors and KOBAYASHI obtained at 29.5 atm total pressure and 450°C the same value of 2 for $\nu(r)$ by a similar experiment⁹⁾. This conclusion that $\nu(r)=2$ excludes the rate-determining step of the dissociative adsorption, admitted that (16) proceeds through the sequence of steps,



where (a) signifies the adsorbed state, inasmuch as the stoichiometric numbers of (17. I_N) and (17. I_H) are 1 and 3 respectively, whereas those of (17. II₁), (17. II₂) and (17. II₃) are equally 2.

We might examine the above conclusion on the basis of the present analysis. ENOMOTO and HORIUTI⁷⁾ have observed the decrease of atomic fraction of N¹⁵ in ammonia in the above equilibrium mixture for determining the backward rate of (16) balanced with its forward rate \bar{r}_e .

The \bar{r}_e is now 0.3 mmHg (NH₃) per hr at 400°C as observed by ENOMOTO and HORIUTI i. e. $0.3 \times n/2 \times 60 \times WP \text{ mol}(\text{N}_2) \text{ min}^{-1} \text{ gm}(\text{cat})^{-1*}$, where 2 in the denominator is the factor converting the rate expressed

7) S. ENOMOTO and J. HORIUTI, This Journal 2, 87 (1953).

8) J. HORIUTI and M. IKUSHIMA, Proc. Imp. Acad. Tokio 15, 39 (1939).

J. HORIUTI, Sc. Papers Inst. Phys. Chem. Res. Tokio 37, 274 (1940).

J. HORIUTI, This Journal 1, 8 (1948).

9) S. ENOMOTO, J. HORIUTI and H. KOBAYASHI, This Journal 3, 185 (1955).

*) The value $0.3/2 \times 60 \times WP$ gives the fraction of nitrogen formed or consumed in one direction per minute per gm catalyst to the total quantity of nitrogen in gas and hence the latter multiplied by n gives the corresponding number of mols.

in the quantity of ammonia to that of nitrogen, n the total number of mols of nitrogen in gas phase, P the partial pressure of nitrogen in mmHg and W the weight of the catalyst before reduction in gm. The n is 2.9×10^{-2} mol, the total amount of gas in gas phase being 2600 cc NTP. Putting 100 mmHg for P and 23 gm for W according to the condition of the experiment, we have 3.2×10^{-8} mol(N₂) min⁻¹ gm(cat)⁻¹ for \bar{r}_e .

It follows on the other hand from the values of \bar{k}_1 and θ that the forward rate of dissociative adsorption per gm at the same condition is $\frac{\bar{k}_1 AP(1-\theta)^2}{W} = 2.1 \times 10^{-5}$ or 9.6×10^{-5} or 1.1×10^{-4} mol(N₂) min⁻¹ gm(cat)⁻¹ i. e. 7×10^2 or 3×10^3 or 3.6×10^3 times as large as the forward or backward rate, according as $N=1.2 \times 10^{-4}$ or 1.2×10^{-3} or 1.2×10^{-2} mol, i. e. that (17. I_N) can by no means determine the rate in confirmation of the conclusion of ENOMOTO and HORIUTI.

Present authors wish to thank Prof. T. KWAN for his kind offer of his unpublished data of sorption.

Summary

1. Observations of sorption of nitrogen on doubly promoted ammonia synthesis catalyst were supplemented and those at 300°C. 400°C and 450°C kinetically analysed.

2. The mechanism of simple dissociative adsorption could not account for the observed kinetics.

3. The mechanism of dissociative adsorption followed by absorption of adsorbed nitrogen atoms by the catalyst fits in quantitatively with the kinetics.

4. The present result of analysis leads to a correct order of magnitude of the number of sites for dissociative adsorption.

5. The present result of analysis leads to an extremely greater rate of dissociative adsorption, accompanying the catalysed synthesis of ammonia, than the forward or backward rate of the latter process as observed by ENOMOTO and HORIUTI by means of nitrogen isotope. This result is consistent with the conclusion arrived at by ENOMOTO

*) The value of θ at equilibrium and hence the forward rate of dissociative adsorption depends, according to (1), on the value of N or of \bar{k}_1 , which is not practically fixed by the linearity of (6) alone; cf. §3.

and HORIUTI that the stoichiometric number of the rate-determining step of the catalysed synthesis of ammonia, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ is two, which excludes the possibility of the dissociative adsorption of nitrogen being the rate-determining step.