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STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP OF AMMONIA SYNTHESIS ON IRON CATALYSTS

Comment on The Papers[1)2)] of C. BOKHOVEN, M. J. GORGELS and P. MARS

By

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(Received February 26, 1962)

Introduction

BOKHOVEN, GORGELS and MARS[1)] have concluded from their experimental results that the stoichiometric number ν_r of the rate-determining step of the catalyzed synthesis of ammonia in the presence of commerical synthetic catalyst is unity as referred to the chemical equation

$$N_2 + 3H_2 = 2NH_3 , \qquad (1)$$

contradicting the previous conclusion of ENOMOTO, HORIUTI and KOBAYASHI[3)] that ν_r is two instead.

BOKHOVEN *et al.*[1)] have passed the gas mixture of nitrogen, hydrogen and ammonia nearly in equilibrium of (1) through the catalyst bed at 429°C and 7.5 atm total pressure. They have observed the rate of (1) as well as that of N^{15}-exchange between ammonia and nitrogen, *i.e.*

$$(N^{15})_{NH_3} = (N^{15})_{N_2} \qquad (2)$$

or that of the exchange reaction

$$N_2^{30} + N_2^{28} = 2N_2^{29} , \qquad (3)$$

where $(N^{15})_{NH_3}$ or $(N^{15})_{N_2}$ denotes the constituent N^{15}-atom of NH_3- or N_2-molecule respectively. They conducted the above experiments in two series*). In the first series they passed the gas mixture nearly in equilibrium of (1) through a catalyst bed and observed the rates of (1) and (2) simultaneously on one and the same catalyst bed in one and the same gas flow. They determined the equilibrium fraction x_e^A of ammonia in the gas mixture, which is required

*) The temperature of the second series experiment mentioned as 425°C in their first issue (Ref. 1) has been amended as 429°C in their second one (Ref. 2).

for the calculation of rate of (1), separately at low space velocity. The evaluation of ν_r by them[1] from the above simultaneous measurements of rates of (1) and (2) is summarized essentially by the equation*)

$$\nu_r = 2\frac{1+3x_e^A}{1+x_e^A}\frac{\log(z_0^A-z_i)/(z_t^A-z_i)}{\log(x_e^A-x_0^A)/(x_e^A-x_t^A)}, \qquad (4)$$

where x^A is the mol fraction of ammonia in the gas mixture, z^A is the N^{15}-atomic fraction in ammonia, suffix 0 or t signifies the particular value at the inlet or the outlet of the catalyst bed and z_i is the value of z^A in equilibrium of (2).

In the second series experiment, they passed the gas mixture nearly in equilibrium of (1) through two series-arranged catalyst beds and measured the rates of (1) and (2) on the first catalyst bed and the rate of (3) on the second one. The stoichiometric number was worked out from the rates of (1) and (2) on the first catalyst bed as well as from the rate of (3) on the second catalyst bed combined with that of (1) on the same catalyst bed, which was derived indirectly, as referred to later, from the rate of (1) observed on the first one. They identified x_e^A and z_i required for the evaluation of ν_r, as seen in (4), respectively with x^A and z^A at the outlet of the second catalyst bed, assuming that both (1) and (2) attained their equilibria there.

HORIUTI and TAKEZAWA[4] and KODERA and TAKEZAWA[5] commented upon their procedure[1] of deriving the stoichiometric number in two points (A) and (B).

(A) As based on their statement[1] that their first series experiment was conducted at 429°C and 7.5 atm total pressure, it follows[4] inevitably from the considerable fluctuation of x_e^A-value as much as 9% for the first series experiment that x_e^A given by them is systematically too low and hence that the correct value of the stoichiometric number may be twice as large as the value given by them.

(B) HORIUTI and TAKEZAWA[3] and KODERA and TAKEZAWA[4] found in some runs of the second series experiment that (2) as well as (3) departs significantly from equilibrium at the outlet of the second catalyst bed, hence their rates may be evaluated simultaneously on one and the same catalyst bed in such gas flow. They have deduced[3][4] from these rates that the rate-determining step is not the dissociative adsorption of nitrogen molecule

$$N_2 \longrightarrow 2N(a), \qquad (5.N)$$

*) This is Eq. (3) of Ref. (4) with its factor $(4/P_e^A+1/P_e^N+9/P_e^H)/(2/P_e^A+1/P_e^N)$, replaced with its equivalence $2(1+3x_e^A)/(1+x_e^A)$, where P_e^A, P_e^N and P_e^H are respectively the partial pressures of ammonia, nitrogen and hydrogen in equilibrium of (1) and $P_e^N : P_e^H = 1:3$. BOKHOVEN *et al.* (Ref. 1 and 2) appear to have used the average of $(2/P^A+1/P^N)$-values at the inlet and outlet of the catalyst bed in place of $(2/P_e^A+1/P_e^N)$ in Eq. (3) of Ref. (4) as judged from the numerical values of ν_r they give; *cf.* Table 1.

resulting in adsorbed nitrogen atoms N(a), but one of the subsequent steps

$$N(a)+H(a) \longrightarrow NH(a)\,, \qquad (5.\,NH)$$

$$NH(a)+H(a) \longrightarrow NH_2(a)\,, \qquad (5.\,NH_2)$$

and

$$NH_2(a)+H(a) \longrightarrow NH_3\,, \qquad (5.\,NH_3)$$

where NH(a) *etc.* are adsorbed intermediates and H(a) is adsorbed hydrogen atom formed by the step

$$H_2 \longrightarrow 2H(a)\,. \qquad (5.\,H)$$

Since the stoichiometric number of (5.N) is unity, whereas that of any of (5.NH), (5.NH_2) and (5.NH_3) is two as referred to the overall reaction (1), it follows that $\nu_r=2$ in conformity with our previous conclusion[3].

In reply to the above comment (A), BOKHOVEN *et al.* amended[2] their statement[1] of the temperature, at which x_e^A was separately observed, that 429°C mentioned in their first issue[1] is just an "approximate" expression of the exact ones, 430.0°C, 423.0°C, 425.0°C *etc.*, each being appropriate, by HABER's formula[6], to one of the considerably fluctuating x_e^A-values. They give[2] exact values of the total pressure near 7.5 atm anew as well each as relevant to one of the exact values of x_e^A.

The amended statement of the exact condition of the x_e^A-measurement would make any sense, if each condition were reproduced with such accuracy in the relevant observation of the rates of (1) and (2). We investigate this point in §1, concluding that the latter proviso is not assured to have been fulfilled in the experimental arrangements of BOKHOVEN *et al.*[1], hence their conclusion[1] $\nu_r=1$ neither reliable just as concluded in the previous papers[4][5].

In reply to our comment (B)[4][5], BOKHOVEN *et al.* maintain[2] that the exchange reaction (2) attained equilibrium practically at the outlet of the second catalyst bed, demonstrating that the ν_r-value deduced from the experimental result on the first catalyst bed is not significantly different whether based on z_i identified with z_i^A at the outlet of the second catalyst bed or with the averaged value of N^{15}-atomic fraction z^N in nitrogen and that z^A in ammonia over the concentration n of nitrogen and that a of ammonia in the gas mixture, as

$$z_i = \frac{2nz^N + az^A}{2n+a}\,, \qquad (6)$$

which must be constant along the gas flow and provide the exact value of N^{15}-atomic fraction in ammonia as well as in nitrogen in the equilibrium of (2), insofar as N^{15} is kinetically identical with N^{14}.

This reply is quite off the point. The argument of (B) is based upon the rate of (2) evaluated on the second catalyst bed by virtue of the departure from its equilibrium at the outlet, but not concerned with the question whether z_t^A of the second catalyst bed be a good substitute for z_i in calculating ν_r from the experimental results on the first catalyst bed.

It is now shown in § 2 that the rate of (1) on the second catalyst bed derived from that on the first catalyst bed is unreliable, hence neither is the value of ν_r deduced from the latter combined with the rate of (3), and in § 3 that the departure of z_t^A in the second catalyst bed from z_i is statistically significant but not within experimental error in some cases of runs of the second series experiment. From the departure thus shown significant, the previous conclusion on the rate-determining step is drawn in § 4 in a straightforward, alternative way in view of the above misunderstandings of the point (B).

BOKHOVEN *et al.* maintain[2], besides, the correctness of their values of x_e^A which leads to $\nu_r=1$, on the ground that the specific rate k_s of (1), *i.e.*

$$k_s = 1/t \cdot \ln(1-x_0^A/x_e^A)/(1-x_t^A/x_e^A) \qquad (7)$$

remains constant on the base of these values of x_e^A irrespective of the distance from equilibrium, where t is the contact time. They appear to try to demonstrate this point in Fig. 2 of their second issue[2], although not traceable, the notations involved being neither defined nor the source of data being specified. It is shown in § 5 that the above criterion is fulfilled much better by the values of x_e^A, which yield $\nu_r=2$ by (4) instead.

Summarizing the above arguments it is concluded again that their inference $\nu_r=1$ is unreliable but their experimental result itself affirms that $\nu_r=2$.

§ 1. Accuracy of ν_r from the First Series Experiment

It is investigated how accurate the condition of x_e^A-measurement is reproduced in x_0^A- and x_t^A-determinations and how much difference in ν_r-value is made by the deviation of the amended "exact" value of x_e^A from its value at the very condition of the latter determinations.

They have, according to their first issue[1], a thermometer in the fluidized bed around the reactor, by which the temperature there, but not inside the reactor, was observed to be kept constant within 1°C. It is hence reasonable to assume that the "exact" temperature of x_e^A-observation deviates from that of x_0^A- and x_t^A-determinations within 1°C, provided that there exists no particular situation which shifts the latter systematically from the former. The total pressure may be taken from the experimental arrangements of BOKHOVEN *et al.* to have been kept constant within 0.1 atm[1].

It has been shown in a previous paper[4]* that x_e^A shifts by $0.0125\,x_e^A$ with 1°C deviation of temperature and by $0.0127\,x_e^A$ with 0.1 atm deviation of the total pressure. It follows that x_e^A may deviate within

$$0.0125\,x_e^A + 0.0127\,x_e^A = 0.0252\,x_e^A$$

from its value appropriate to the condition of x_0^A- and x_t^A-determinations, if the above proviso were fulfilled.

The two runs of their first series experiment[1] referred to in Table 1 have been conducted on one and the same catalyst bed in such gas flow, which is essential to a consistent determination of ν_r, if the catalytic activity is sensitively changed by catalytic poison as they state[2]. Table 1 shows in the third row the values x_e^A(B) of x_e^A underlying the calculation of BOKHOVEN *et al.*[1] as computed from x_t^A and x_t^A/x_e^A given by them, in the fourth row the values of ν_r given by them[1]**, and in the second last row the ν_r-values calculated from x_e^A(B) by (4). The last row gives the values of ν_r computed by (4) from the values of x_e^A each increased by 2.5% from x_e^A(B) according to the above.

TABLE 1. Calculation of ν_r from Runs of Series I

Space Velocity hr^{-1}	12,100	12,120
Catalyst	I	II
The value x_e^A(B) of x_e^A underlying the calculation of BOKHOVEN *et al.*	0.0215	0.0226
ν_r given by BOKHOVEN *et al.*	1.05	0.87
ν_r by (4) for $x_e^A = x_e^A$(B)	1.16	0.95
ν_r by (4) for $x_e^A = x_e^A$(B)×1.0252	1.63	1.39

Table 1 shows that the value of ν_r is extremely sensitive to the fluctuation of x_e^A or to the deviation of the experimental condition of x_e^A-measurement from that of x_0^A- and x_t^A-determinations. A few percent deviation of x_e^A-value is

*) It has been shown in Ref. 4 that the relative deviation $\delta x_e^A/x_e^A$ of x_e^A is given as

$$\frac{\delta x_e^A}{x_e^A} = \frac{1-x_e^A}{1+x_e^A}\left\{\frac{\delta K}{2K} + \frac{\delta P}{P} + \frac{3-\lambda}{2(1+\lambda)}\,\frac{\delta\lambda}{\lambda}\right\},$$

where $\delta K/K$ is the relative deviation of the equilibrium constant K of (1) due to 1°C deviation of temperature and $\delta P/P$ or $\delta\lambda/\lambda$ is that of the total pressure P or the mixing ratio λ of hydrogen to nitrogen. The last term in the parentheses { } vanishes for $\lambda=3$. The relative deviation $(1-x_e^A)/(1+x_e^A)\cdot\delta K/2K$ of x_e^A caused by 1°C deviation of temperature is 0.0125 according to the HABER's formula (Ref. 6), whereas that $(1-x_e^A)/(1+x_e^A)\cdot\delta P/P$ of x_e^A due to 0.1 atm deviation of total pressure is 0.0127 as mentioned respectively in the text.

**) *Cf.* footnote on p. 2.

sufficient to turn the conclusion from $\nu_r=2$ into $\nu_r=1$ in the procedure of BOKHOVEN *et al.*[1)2)]

The above argument is based on the proviso that there exists no systematic deviation of the condition of x_e^A-measurement from that of x_0^A- and x_t^A-determinations, which is not, however, assured as shown below. In the case of x_0^A- and x_t^A-determinations, the gas mixture is passed through the catalyst bed at more than ten times as much space valocity as in the case of x_e^A-measurement[1)2)]. The gas mixture should be supplied with the heat of the amount of *ca.* $7\times 400=2800$ cal/mol gas mixture in order to attain the temperature of the catalyst bed. This want of heat is only partly compensated by the supply of heat of formation 12,000 cal/mol ammonia times the fraction 0.02 of ammonia, *i.e.* 240 cal/mol gas mixture, which begins at the inlet and ends at the outlet of the catalyst bed. It follows that the temperature in the catalyst bed may be systematically lower than in the fluidized bed especially in the case of x_0^A- and x_t^A-determinations, hence that the "exact" x_e^A-value[2)] may be more or less systematically lower than that appropriate to the latter determinations. This difficulty is of course avoided by an efficient preheating, which is not however controlled in the experimental arrangements of BOKHOVEN *et al.*[1)], thermometer being not inside the catalyst bed[1)].

Since the value of x_e^A appropriate to the x_0^A- and x_t^A-determinations may be systematically greater than that given by BOKHOVEN *et al.*[2)] by this cause and the ν_r-value increases sensitively with increase of x_e^A according to (4), the correct value of ν_r may be still greater than that given in the last row of Table 1, although not numerically estimated. That the ν_r-value given by BOKHOVEN *et al.*[1)2)] is too low still persists inspite of their amended statements of x_e^A-values[2)].

This conclusion is unaffected, if the degree of conversion be over 0.999 in their x_e^A-measurement as they state[2)], since this does not mean, if at all, that x_e^A-value they give lies so close to that at the very condition of the x_0^A- and x_t^A-determinations. Besides, this calculation of the degree of conversion is itself illegitimate under the condition, where the catalytic activity is sensitively changed by catalytic poison as they state[2)], since it must necessarily be calculated from the k_s-value determined by a run separate from that appropriate to the x_e^A-measurement.

§ 2. Comment on the Second Series Experiments of BOKHOVEN *et al.*[1)2)]

The second series experiments of BOKHOVEN *et al.*[1)2)] have been carried out, as mentioned in the introduction, by passing the gas mixture nearly in

equilibrium of (1) through the two series-arranged catalyst beds and by observing the rates of (1) and (2) on the first catalyst bed and the rate of (3) on the second catalyst bed. They have evaluated ν_r from the observations on the first catalyst bed as in the case of the first series experiment and from the rate of (3) on the second catalyst bed as well by combining it with k_s on the second catalyst bed estimated indirectly from that observed on the first catalyst bed.

The same argument as that developed in the foregoing section holds true with the evaluation of ν_r from the rates of (1) and (2) on the first catalyst bed, leading to the same conclusion that the ν_r-value near unity as given by them[1] is unreliable because their value of x_e^A is liable to be too low. Their argument for the pertinence of their x_e^A-value[2] is commented upon in §5. Their second procedure of the ν_r-evaluation will be discussed in this section.

BOKHOVEN *et al.* state[2] that "the determination of the stoichiometric number is not influenced by the presence of poison, if any, because k_{synth} and k_{exchange} are determined in the same gas stream". The k_{synth} and k_{exchange} are to be understood as the specific rates of (1) and (3) from the context, although not defined[1)2)]. Their statement above cannot be true now, since the first catalyst may be preferentially and incontrollably poisoned acting as a getter. These rates may be taken, however, particularly to have been observed without incontrollable effect of catalytic poison, if based on their statement[1] that "the activities of the catalysts remain constant for weeks under the conditions used in the experiments described here". In such a case, however, we need only to observe the rates of (1) and (3) on one and the same catalyst bed separately as did by HORIUTI *et al.*[3] rather than circuitously to derive the rate of (1) on the second catalyst bed from that observed on the first catalyst bed by a procedure not reliable as shown below.

They observed the rate constant k_T of the TEMKIN-PYZHEV's rate equation on the first and the second catalyst bed, which will be denoted by k_T(I) and k_T(II) respectively. The k_s on the second catalyst bed was now evaluated as the k_s observed on the first catalyst bed multiplied by the ratio k_T(II)/k_T(I). It is true that k_T reduces to k_s, when the gas mixture is sufficiently near equilibrium of (1)[5]. This procedure would in consequence be sound, if we know the ratio k_T(II)/k_T(I) at the very condition of the second series experiment, where the gas mixture was kept close to the equilibrium of (1) at space velocity as low as *ca.* 500 hr^{-1} as referred to the second catalyst bed. According to their experimental results, however, the k_T(I) and k_T(II) are observed at large space velocity in one and the same gas flow and more than quadrupled, as the space velocity decreases from 22,580 to 16,290 hr^{-1} as referred to the second catalyst bed, while the ratio k_T(II)/k_T(I) remains marvellously constant over the

range. It follows that the TEMKIN and PYZHEV's rate equation does not hold at all. The constant ratio $k_T(\mathrm{II})/k_T(\mathrm{I})$ is thus purely empirical.

The empirical constancy of $k_T(\mathrm{II})/k_T(\mathrm{I})$ observed over the range of the large velocity is now extrapolated as far as down to *ca.* 500 hr^{-1} as referred to the second catalyst bed. The empirical rule so far extrapolated toward the unobserved region is by no means assured, hence the ν_r-value determined on its basis neither.

§ 3. Equilibrium of (2) on the Second Catalyst Bed of the Second Series Experiment

BOKHOVEN *et al.*[1] maintain that the reaction (2) attained equilibrium at the outlet of the second catalyst bed. Table 2 shows the values of z_i calculated by (6) from the data given by BOKHOVEN *et al.*[1] respectively at the "inlet" of the first catalyst bed, the "middle" between the first and the second catalyst beds and the "outlet" of the second catalyst bed, which should be coincident with each other within experimental errors for one and the same gas flow.

TABLE 2. z_i at Different Places and z_t^{A} at the Outlet

Runs		1.2	1.3	1.4	2.2	2.3	2.4
$100\,z_i$	"inlet"	1.068	1.046	1.041	1.166	1.169	1.180
	"middle"	1.093	1.056	1.043	1.169	1.170	1.166
	"outlet"	1.063	1.059	1.065	1.180	1.176	1.179
	"mean"	1.075 ± 0.0093	1.054 ± 0.0039	1.050 ± 0.0077	1.172 ± 0.0043	1.172 ± 0.0029	1.175 ± 0.0045
$100\,z_t^{\mathrm{A}}$	"outlet"	1.095	1.041	1.069	1.100	1.086	1.110

The "mean" is that of the three observations of z_i for each run and the figures following the ± sign is the standard deviation $\sqrt{\sum v^2/6}$ of the "mean", where v is the difference between the individual z_i-value and the "mean". The z_t^{A} is the value of z^{A} at the "outlet" of the second catalyst bed. In the first three runs 1.2, 1.3 and 1.4, z_t^{A} lies near z_i but in the remaining three runs z_t^{A} does appreciably below z_i.

We investigate now the significance of the difference $z_i - z_t^{\mathrm{A}}$ in the case of the last three runs. The standard deviation of $100\,z_t^{\mathrm{A}}$ must be less than 0.01, since, if otherwise, more than 61%*) of $100\,z_t^{\mathrm{A}}$-observations will have

*) This is the probability P that the ratio x of the deviation to the standard deviation exceeds 0.005/0.010=0.5 according to Table I on p. 80 of Ref. 7.

positive or negative deviation exceeding 0.005[7], contradicting their statement[1] that $100\,z_t^A$-observation is reproducible within 0.01. The upper bound to the standard deviation $100\,\sigma(z_i-z_t^A)$ of $100(z_i-z_t^A)$ is now given in the fourth row of Table 3 for the respective runs as calculated by the equation

$$\sigma(z_i-z_t^A)^2=\sigma(z_i)^2+\sigma(z_t^A)^2,$$

TABLE 3. Statistical Significance of $z_i-z_t^A$

Runs	2.2	2.3	2.4
$100\ \sigma(z_i)$	0.0043	0.0029	0.0045
$100\ \sigma(z_t^A)$	<0.01	<0.01	<0.01
$100\ \sigma(z_i-z_t^A)$	<0.0109	<0.0104	<0.0110
$100\ (z_i-z_t^A)$	0.072	0.086	0.065
$x=\dfrac{z_i-z_t^A}{\sigma(z_i-z_t^A)}$	>6.6	>8.3	>5.9
Probability P*)	$<10^{-10}$	$<10^{-10}$	$<10^{-8}$

*) *Cf.* Table II on p. 80 of Ref. 7.

where $\sigma(z_i)$ and $\sigma(z_t^A)$ are standard deviations of z_i and z_t^A respectively. The third last row shows $z_i-z_t^A$, which is the difference of the "mean" of z_i and z_t^A in Table 2 and the last row gives the probability[7] that the normally distributed observations of $z_i-z_t^A$ will have negative or positive deviation exceeding its value in the third last row. It is concluded from this amount of probability that $z_i-z_t^A$ in Table 3 is significant.

BOKHOVEN *et al.* maintain[2] that the equilibrium of (2) is practically attained on the second catalyst bed and hence attribute[2] the difference $z_i-z_t^A$ to an insignificant experimental error on the ground that "the experimental value of $k_{N_2^{30}+NH_3}$ and the space velocity applied lead to a degree of conversion on the second catalyst bed which is greater than 0.99". They define $k_{N_2^{30}+NH_3}$ neither in their first issue[1] nor in the second one[2] but the context indicates that it is $k_{e,I}\equiv 1/t\cdot\ln(z_i-z_0^A)/(z_i-z_t^A)$, which is directly observed on the first catalyst bed. Their result mentioned above is reproduced by evaluating $k_{e,I}$ on the second catalyst bed as the product of $k_{e,I}$ on the first catalyst bed and the ratio $k_T(\mathrm{II})/k_T(\mathrm{I})$ dealt with in §2 and calculating the appropriate value of the degree of conversion z_t^A/z_i from the value of $k_{e,I}$ and the space velocity $1/t$ respectively on the second catalyst bed. The similar procedure of k_s-evaluation on the second catalyst bed was shown in §2 to be unreliable because of the far extended extrapolation of the empirical rule. The situation is expected still worse for $k_{e,I}$, since the constancy of the ratio of its value for the first catalyst bed

to that for the second one is not empirically verified even for the limited range of space velocity.

We have no reason to repudiate the direct evidence for the significant departure $z_i - z_t^A$ from equilibrium because of the indirect as well as unreliable inference above.

§ 4. Rate-Determining Step Deduced from $z_i - z_t^A$

It would be worthwhile to present here an alternative straightforward deduction of the rate-determining step from the difference $z_i - z_t^A$ shown significant in the foregoing section, in view of the answer[2], quite off the point, to the comment (B).

Assuming with BOKHOVEN *et al.*[1] that the equilibrium of (1) is practically attained on the second catalyst bed in their second series experiment, we have

$$\vec{V}_{N,e} z_2^N > -n_e dz_2^N/dt ,$$

where $\vec{V}_{N,e}$ is the unidirectional forward rate of (5.N), z_2^N the mol fraction of N_2^{30} in nitrogen gas, hence $\vec{V}_{N,e} z_2^N$ is the unidirectional forward rate of N_2^{30} getting into the step (5.*N*) and $-n_e dz_2^N/dt$ is the overall rate of decrease of N_2^{30}, which is less than the unidirectional forward rate $\vec{V}_{N,e} z_2^N$ by the unidirectional backward one as stated by the above inequality. It follows that

$$\vec{V}_{N,e} > (n_e/t) \ln z_{2,0}^N / z_{2,t}^N , \qquad (8)$$

where $z_{2,0}^N$ or $z_{2,t}^N$ is the value of z_2^N at the inlet or the outlet respectively.

We have on the other hand for the unidirectional forward rate $\vec{V}_e$ of the overall reaction (1)

$$a_e \frac{dz^A}{dt} = 2\vec{V}_e (z^N - z^A) ,$$

inasmuch as two nitrogen atoms are transferred from nitrogen to ammonia for every forward act of (1). It follows from the above equation and (6), eliminating z^N from them and integrating

$$\vec{V}_e = \frac{a_e n_e}{t(a_e + 2n_e)} \ln \frac{z_i - z_0^A}{z_i - z_t^A} , \qquad (9)$$

hence from (8) and (9)

$$\frac{\vec{V}_{N,e}}{\vec{V}_e} > \frac{(1 + 2n_e/a_e) \ln z_{2,0}^N / z_2^N}{\ln (z_i - z_0^A)/(z_i - z_t^A)} , \qquad (10)$$

noting that t in (8) and (9) is the one and the same contact time on the second catalyst bed.

The ratio $\vec{V}_{N,e}/\vec{V}_e$ should now be either practically equal to unity or definitely greater than unity according as the step (5.N) is rate-determining or not. Table 4 shows the lower bound to $\vec{V}_{N,e}/\vec{V}_e$ calculated by (10) from the basic data given there; among them $2n_e/a_e$ is calculated from the mol fraction x_t^A of ammonia at the outlet of the second catalyst bed by the equation

$$2n_e/a_e = (1-x_t^A)/2x_t^A ,$$

$z_i - z_t^A$ is transferred from Table 3 and $z_i - z_0^A$ is the difference of the "mean" of z_i in Table 2 and the "N^{15} in NH_3 at middle" given in Table 2 of BOKHOVEN *et al.*[1]

Since $\vec{V}_{N,e}$ is greater than $\vec{V}_e$ by a factor of *ca.* 10 or more for the runs of significant $z_i - z_t^A$, (5.N) cannot be the rate-determining step.

TABLE 4. The Lower Bound to $\vec{V}_{N,e}/\vec{V}_e$

Runs	2.2	2.3	2.4
$2n_e/a_e$	23.2	23.1	23.1
$100\ z_{2,0}^N$	0.512	0.508	0.504
$100\ z_{2,t}^N$	0.263	0.255	0.256
$100\ (z_i - z_0^A)$	0.497	0.511	0.504
$100\ (z_i - z_t^A)$	0.072	0.086	0.065
$\vec{V}_{N,e}/\vec{V}_e$	>8.3	>9.3	>8.0

§ 5. The Criterion of x_e^A-value

BOKHOVEN *et al.*[2] appear to maintain the constancy of k_s-value as the criterion of the correct x_e^A-value involved in the expression (7) of k_s as mentioned in the introduction. The x_e^A-value given by BOKHOVEN *et al.*[1], which leads to $\nu_r = 1$ by (4), is possibly too low systematically as shown in §1. It is now demonstrated that the value of x_e^A, which gives $\nu_r = 2$ instead by (4), fulfils the criterion much better than the lower value leading to $\nu_r = 1$.

The above criterion is employed for the examination of runs referred to in Tables 3 and 4, which are relevant to the present discussion and conducted under the condition fitted best to the examination; that is, the temperature and the total pressure of x_e^A-measurement are respectively perfectly constant, as they state[2] and "the activities of the catalyst remain constant for weeks……"[1], so that the fluctuation of k_s due to temperature and pressure variation or catalytic poison is best eliminated.

The second and the third rows of Table 5 show the values x_e^A(B) and k_s(B)

TABLE 5. Constancy of k_s as a Criterion of x_e^A

Runs	2.2	2.3	2.4
100 x_e^A(B)	2.114	2.119	2.120
k_s (B)	13700	14450	11640
100 x_e^A for $\nu_r=2$	2.331	2.385	2.288
k_s	6980	6580	6820

respectively of x_e^A and k_s given by BOKHOVEN *et al.*[1] for the first catalyst bed. The fourth row gives the values of x_e^A calculated by (4) for $\nu_r=2$ in accordance with the conclusion of the foregoing section using the values of x_0^A, x_t^A, z_0^A and z_t^A given by BOKHOVEN *et al.*[1] for the first catalyst bed and the "mean" of z_i in Table 2. We see from the Table that the x_e^A appropriate to $\nu_r=2$ fulfils the criterion much better than the x_e^A(B) does.

§ 6. Conclusion

As shown above, the inference $\nu_r=1$ of BOKHOVEN *et al.*[1][2] is not reliable, whereas their experimental results lead consistently to the conclusion in conformity with our previous one[3], $\nu_r=2$.

This conclusion is verified by the experimental result of SCHOLTEN and ZWIETERING[8] that the rate of adsorption of nitrogen alone on the synthetic catalyst is equal to the rate of (1) on the same catalyst, since according to the recent result of TAMARU[9] the rate of (5.N) is appreciably accelerated by the presence of hydrogen, hence the step (5.N) cannot be the rate-determining step at the condition of the synthesis. Since the hydrogen adsorption (5.H) is a still faster step[10][11], our inevitable conclusion as based on the set (5) of steps responsible for the occurence of (1) is that the rate-determining step is one of (5.NH), (5.NH_2) and (5.NH_3), for which the stoichiometric number is commonly 2.

References

1) C. BOKHOVEN, M. J. GORGELS and P. MARS, Trans. Faraday Soc., **55**, 315 (1959).
2) C. BOKHOVEN, M. J. GORGELS and P. MARS, This Journal, **9**, 237 (1961).
3) S. ENOMOTO and J. HORIUTI, Proc. Japan Acad. Tokio, **28**, 493, 499 (1952); This Journal, **2**, 87 (1951-3). S. ENOMOTO, J. HORIUTI and H. KOBAYASHI, *ibid.*, **3**, 185 (1953-5).
4) J. HORIUTI and N. TAKEZAWA, *ibid.*, **8**, 127 (1960).
5) T. KODERA and N. TAKEZAWA, *ibid*, **8**, 157 (1960).
6) F. HABER, Z. Elektrochem., **20**, 597 (1914).
7) R. A. FISHER, *Statistical Methods for Research Workers*, 1936, Table I and II, p. 80.

8) J. J. F. SCHOLTEN and P. ZWIETERING, Trans. Faraday Soc., **53**, 1363 (1957).
9) K. TAMARU, *Transactions of the Second International Congress on Catalysis* (Paris) **1**, 325 (1960).
10) H. S. TAYLOR and J. C. JUNGERS, J. Am. Chem. Soc., **57**, 660 (1935).
11) S. ENOMOTO, "*Shokubai*" (Catalyst), **8**, 47 (1952), **14**, 87 (1957).