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MECHANISM OF AMMONIA SYNTHESIS REACTION

Comment on the Paper of BOKHOVEN
GORGELS and MARS¹⁾

By

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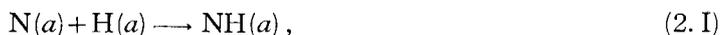
Introduction

HORIUTI *et al.*²⁾⁻⁶⁾ have previously introduced the concept of the stoichiometric number ν and determined that $\nu(r)$ of the rate-determining step r of the hydrogen electrode reaction on platinum near the electrochemical equilibrium to be unity. A similar concept was put forward by BORESKOV⁷⁾ in terms of his molecularity of a molecule involved in a overall reaction.

The stoichiometric number $\nu(r)$ of the catalyzed ammonia synthesis reaction



in the presence of the doubly promoted iron catalyst has been determined at 2 by ENOMOTO, HORIUTI and KOBAYASHI^{8),9)}. This result excludes the rate-determining step of the chemisorption of nitrogen, which has long been taken as established¹⁰⁾⁻¹³⁾, insofar as the synthesis reaction (1) proceeds through the sequence of steps,

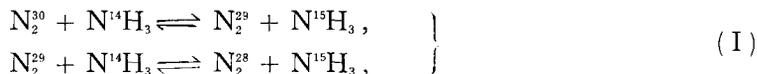
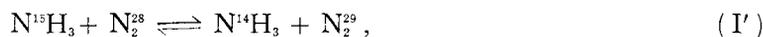


where $\text{N}(a)$ *etc.* is the nitrogen atom *etc.* adsorbed on the catalyst. HORIUTI and TOYOSHIMA^{14),15)} concluded that the rate-determining step was (2. I) in accordance with the above results^{8),9)} by the analysis of their observation on the catalyzed decomposition of ammonia in the presence of the same catalyst.

However, BOKHOVEN, GORGELS and MARS¹⁾ have recently concluded that $\nu(r)=1$, contradicting the above results, by the comparison of the rate V of

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the ammonia synthesis near equilibrium with the rate of one ~f the three exchange reactions



HORIUTI and one of the present authors¹⁶⁾ have shown that the above conclusion of BOKHOVEN *et al.*¹⁾ drawn from the comparison of V with the rate of (I') or (I) is erroneous, mainly because of their values of the equilibrium concentration of ammonia, which were determined systematically too low. These authors¹⁶⁾ have shown that the $\nu(r)=1$ concluded by BOKHOVEN *et al.*¹⁾ is, as a matter of fact, a lower bound to the true value of $\nu(r)$ owing to the circumstances mentioned. They have shown further from the detailed analysis of the experimental results of BOKHOVEN *et al.*¹⁾ on the above exchange reactions that the rate-determining step of (1) is not (2.N) but one of the last three steps (2. I), (2. II) and (2. III) in conformity with the previous conclusion of ENOMOTO, HORIUTI and KOBAYASHI^{8),9)} and HORIUTI and TOYOSHIMA^{14),15)}.

It is now of interest to investigate the same conclusion of BOKHOVEN *et al.* that $\nu(r)=1$, deduced from the comparison of V with the rate of the exchange reaction (II). It is shown below that their procedure of drawing this conclusion is irrelevant as well, while an alternative diagnosis not suffering from this irrelevance leads to the same conclusion as arrived at by HORIUTI and one of the present authors¹⁶⁾.

§ 1. Investigation of the Procedure of BOKHOVEN *et al.*¹⁾

BOKHOVEN *et al.*¹⁾ allowed 1:3 mixture of nitrogen and hydrogen containing an amount of ammonia less than that at the equilibrium of (1) to flow through the beds of the doubly promoted synthetic catalyst at 7.5 atm. total pressure. In their second series experiment, which we are going to deal with, they¹⁾ allowed the gas mixture to flow through the two portions of the catalyst, I and II, in series, and observed the contents of N_2^{30} , N_2^{29} , N^{15}H_3 and ammonia as a whole between the two portions as well as at the outlet of the second one.

BOKHOVEN *et al.*¹⁾ base their determination of $\nu(r)$ with reference to the exchange reaction (II) on the established expression of the stoichiometric number^{16),17)}, *i. e.*

$$\nu(r) = (\bar{V}_e/k_s)(4/a_e + 1/n_e + 9/h_e) \quad (3)$$

at the equilibrium of (1), where \bar{V}_e is the unidirectional forward rate of (1) and a_e , n_e or h_e is the total number of mols of ammonia, nitrogen or hydrogen contained in a definite part* of the gas mixture conveyed through the portion of the catalyst, the suffix e specifying the quantities at the equilibrium of (1). The factor k_s is the rate constant of (1), expressed in the neighbourhood of its equilibrium as

$$k_s = (1/t) \ln \left[(a_e - a_0) / (a_e - a_t) \right], \quad (4)$$

where a_0 or a_t is the total number of mols of ammonia comprized in the definite part of the gas mixture at the beginning or after time t respectively of its contact with the catalyst.

They have determined \bar{V}_e , as they state, from the experimental result of the exchange reaction (II) observed on the second portion of the catalyst, although the procedure of the determination is not explicitly stated. To find $\nu(r)$, the value of k_s in (3) must also be determined with reference to the same portion of the catalyst. This factor k_s can not however be evaluated as seen from (4), if the synthesis reaction (1) were practically in equilibrium at the outlet of the second portion as assumed by BOKHOVEN *et al.*¹¹ They derived k_s required alternatively as the corresponding quantity $k_{s,I}$ observed on the first portion multiplied by the ratio of activity of the second portion in terms of the rate constant of TEMKIN-PYZHEV's rate equation¹² to that of the first one. This procedure is reasonable, provided that TEMKIN-PYZHEV's rate equation¹² fits in adequately with their experimental results¹¹.

The forward or the backward unidirectional rate \bar{V} or \bar{V} is, according to TEMKIN and PYZHEV¹², inversely or directly proportional to a respectively. As n and h are practically constant at the present experimental condition, we have

$$\bar{V} = \bar{k}'_s/a, \quad \bar{V} = \bar{k}'_s a,$$

where \bar{k}'_s or \bar{k}'_s is the appropriate rate constant. Since $\bar{V}_e = \bar{V}_e$, we have

$$\bar{k}'_s = \bar{k}'_s / (a_e)^2,$$

so that

$$V = \bar{V} - \bar{V} = (\bar{k}'_s/a) [1 - (a/a_e)^2].$$

Expressing $2V$ as da/dt , we have

$$da/dt = (2\bar{k}'_s/a) [1 - (a/a_e)^2]$$

*) The definite part of the gas mixture is subject to a constant pressure rather than to a constant volume in the experiment of BOKHOVEN *et al.* (Ref. 1), whereas (3) is appropriate to the constant volume (Ref. 17). The error committed by this substitution is, however, trifling (Ref. 16).

or by integration

$$\ln \left[\left\{ 1 - (a_0/a_e)^2 \right\} / \left\{ 1 - (a_t/a_e)^2 \right\} \right] = 4\vec{k}'_s t / (a_e)^2. \quad (5)$$

In the neighbourhood of the equilibrium of (1), where both a_0 and a_t are nearly equal to a_e , we have from the above equation approximately

$$\ln \left[(a_e - a_0) / (a_e - a_t) \right] = 4\vec{k}'_s t / (a_e)^2, \quad (6)$$

which conforms to (4) with

$$k_s = 4\vec{k}'_s / (a_e)^2. \quad (7)$$

The rate constant k_s of the second portion was now determined indirectly¹⁾, as mentioned above, from the observation of the rate constant $k_{s,I}$ of the first portion as

$$k_s = k_{s,I} \vec{k}'_{s,II} / \vec{k}'_{s,I}$$

in accordance with (7), where $\vec{k}'_{s,I}$ or $\vec{k}'_{s,II}$ is the value of \vec{k}'_s respectively appropriate to the first or the second portion, which was evaluated according to (5) at the condition sufficiently remote from the equilibrium of (1).

Table 1 shows the applicability of TEMKIN-PYZHEV's rate equation¹²⁾ to the experimental results of BOKHOVEN *et al.*¹⁾, on which the above procedure of BOKHOVEN *et al.*¹⁾ is based. Each row of the Table represents the experimental result of a run, in which the gas mixture was passed through the portions, I and II, in series. The first and the third columns show the space velocities of this gas flow as referred to the respective portions.

TABLE 1. Applicability of TEMKIN-PYZHEV's Rate Equation¹²⁾

Portion I		Portion II	
Space velocity cc NTP cc Catalyst · hr	$\vec{k}'_{s,I}$ hr ⁻¹	Space velocity cc NTP cc Catalyst · hr	$\vec{k}'_{s,II}$ hr ⁻¹
489,300	5,635	22,580	7,410
524,500	7,250	23,000	8,610
524,500	7,730	23,000	9,110
372,400	22,640	16,280	26,650
372,700	22,940	16,290	27,670

Eq. (5) requires that $\vec{k}'_{s,I}$ or $\vec{k}'_{s,II}$ should remain respectively constant independent of the space velocity or the contact time t . This is badly contradicted by the experimental results as shown in Table 1. The ratio $\vec{k}'_{s,I} / \vec{k}'_{s,II}$ is remarkably constant as shown by BOKHOVEN *et al.*¹⁾, if $\vec{k}'_{s,I}$ and $\vec{k}'_{s,II}$ are referred

to the same run, but we have no reasonable ground to restrict the ratio to such particular combinations of $\bar{k}'_{s,I}$ and $\bar{k}'_{s,II}$. The procedure of BOKHOVEN *et al.*¹⁾ is, in consequence, unreliable in this regard, too, similarly as in their determination of $\nu(r)$ from the comparison of V with the rate of (I') or (I)¹⁶⁾.

§ 2. Alternative Diagnosis of the Rate-Determining Step.

HORIUTI and one of the present authors¹⁶⁾ have shown by the detailed analysis of the experimental result of the isotopic exchange over the second portion by BOKHOVEN *et al.*¹⁾, allowing for the deviation from the equilibrium of (1) and for the variation of the overall atomic fraction of N¹⁵ in nitrogen with time, that the rate-determining step is one of the last three steps of (2) rather than (2.N), contradicting the conclusion of BOKHOVEN *et al.*¹⁾ Here will be given an alternative diagnosis, admitting the equilibrium of (1) practically attained over the second portion^{*)}.

The overall unidirectional rate \bar{V}_e at the equilibrium of (1) is given as^{**)}

$$1/\bar{V}_e = 1/\bar{V}_{1,e} + 1/\bar{V}_{2,e}, \quad (8. a)$$

where^{***)}

$$\bar{V}_{2,e} = (1/\bar{V}_{I,e} + 1/\bar{V}_{II,e} + 1/\bar{V}_{III,e})^{-1} \quad (8. b)$$

is the unidirectional forward rate of N(*a*) converted into NH₃, divided by the common stoichiometric number 2 of the last three steps of (2) involved. The quantities $\bar{V}_{I,e}$, $\bar{V}_{II,e}$ and $\bar{V}_{III,e}$ are respectively the forward rates of (2.I), (2.II) and (2.III) each divided by their common stoichiometric number 2. We see from (8) that

$$\gamma \equiv \bar{V}_{1,e}/\bar{V}_e \quad (9)$$

is almost equal to or much greater than unity, according as (2.N) or one of the last three steps of (2) is rate-determining. It has already been established that (2.H) is not the rate-determining step^{17),18)}. The value of γ providing the criterion of the rate-determining step is now located as follows with regard to the experimental results of BOKHOVEN *et al.*¹⁾ on the second portion of the catalyst.

*) The effect of the deviation from the equilibrium of (1) on the conclusion proved rather trifling (Ref. 16).

**) At the steady state, a portion of N(*a*) coming from N₂ is converted further into NH₃ at the rate $2\bar{V}_{2,e}$, whereas the rest turns back to N₂ at the rate $2\bar{V}_{1,e}$. The resultant rate of the unidirectional conversion \bar{V}_e of N₂ toward NH₃ equals in consequence $\bar{V}_{1,e}\bar{V}_{2,e}/(\bar{V}_{1,e} + \bar{V}_{2,e})$, or we have (8.a).

***) Eq. (11) of Ref. 16 reduces to this form at the equilibrium of (1), where $\bar{V}_{I,e} = \bar{V}_{I,e}$, $\bar{V}_{II,e} = \bar{V}_{II,e}$ and $\bar{V}_{III,e} = \bar{V}_{III,e}$.

The unidirectional rate $\bar{V}_{1,e}^{\uparrow}$ in (9) is given in terms of the mol fraction z_2^N or z_1^N respectively of N_2^{30} or N_2^{29} in nitrogen and of the atomic fraction $z^{N(a)}$ of N^{15} in $N(a)$, as^{*})

$$n_e(dz_2^N/dt) = \bar{V}_{1,e}^{\uparrow} [(z^{N(a)})^2 - z_2^N], \quad (10. a)$$

$$n_e(dz_1^N/dt) = \bar{V}_{1,e}^{\uparrow} [2z^{N(a)}(1 - z^{N(a)}) - z_1^N]. \quad (10. b)$$

These equations may be integrated to evaluate $\bar{V}_{1,e}^{\uparrow}$ by expressing $z^{N(a)}$ as a function of time t as did in the detailed analysis of HORIUTI and one of the present authors¹⁶⁾. The present authors inferred, however, alternatively as follows for arriving straightforward at the criterion mentioned.

We have from (10. a)

$$n_e(dz_2^N/dt) > -\bar{V}_{1,e}^{\uparrow} z_2^N,$$

inasmuch as both $\bar{V}_{1,e}^{\uparrow}$ and $(z^{N(a)})^2$ are positive, hence

$$-n_e \int_0^t dz_2^N/z_2^N < \bar{V}_{1,e}^{\uparrow} \int_0^t dt$$

or

$$(n_e/t) \ln(z_{2,0}^N/z_{2,t}^N) < \bar{V}_{1,e}^{\uparrow},$$

where the suffix 0 or t signifies the value at the beginning or after time t of contact of the definite gas mixture with the catalyst as in what follows. The above equation leads, with reference to (9), to the relation

$$\gamma_L < \gamma, \quad (11. a)$$

where

$$\gamma_L = (n_e/t\bar{V}_e) \ln(z_{2,0}^N/z_{2,t}^N) \quad (11. b)$$

is a lower bound to γ .

The rate \bar{V}_e in (9) or in (11. b) is determined from the experimental data as follows. Eq. (10) leads to the equation

$$n_e(dz^N/dt) = \bar{V}_{1,e}^{\uparrow} (z^{N(a)} - z^N), \quad (12. a)$$

where

$$z^N = z_2^N + z_1^N/2 \quad (12. b)$$

is the overall atomic fraction of N^{15} in nitrogen. Either side of (12. a) gives the half of the rate of transition of N^{15} from $N(a)$ to N_2 . The rate of transition of N^{15} from $N(a)$ to NH_3 , *i. e.* $a_e(dz^A/dt)$ is given, on the other hand, in terms of $\bar{V}_{2,e}$, as

*) Cf. Eq. (17) of Ref. 16.

$$a_e(dz^A/dt) = 2\bar{V}_{2,e}^{\rightarrow}(z^{N(a)} - z^A), \quad (13)$$

where z^A is the atomic fraction of N^{15} in ammonia. The steady condition with respect to N^{15} in $N(a)$ is now

$$2n_e(dz^N/dt) + a_e(dz^A/dt) = 0$$

or according to (12.a) and (13)

$$\bar{V}_{1,e}^{\rightarrow}(z^{N(a)} - z^N) + \bar{V}_{2,e}^{\rightarrow}(z^{N(a)} - z^A) = 0,$$

hence

$$z^{N(a)} = (\bar{V}_{1,e}^{\rightarrow}z^N + \bar{V}_{2,e}^{\rightarrow}z^A)/(\bar{V}_{1,e}^{\rightarrow} + \bar{V}_{2,e}^{\rightarrow}). \quad (14)$$

Substituting $z^{N(a)}$ from (14) into (13), we have referring to (8.a)

$$a_e(dz^A/dt) = 2\bar{V}_e^{\rightarrow}(z^N - z^A). \quad (15)$$

The atomic fraction z^N and z^A are related with the average atomic fraction z_i , which is constant for a definite gas mixture, as

$$z_i = (2n_e z^N + a_e z^A)/(2n_e + a_e). \quad (16)$$

Eliminating z^N from (15) and (16), we have

$$dz^A/dt = \bar{V}_e^{\rightarrow}(2/a_e + 1/n_e)(z_i - z^A)$$

or by integration

$$\bar{V}_e^{\rightarrow} = \frac{a_e n_e \ln [(z_i - z_0^A)/(z_i - z_t^A)]}{(2n_e + a_e)t}. \quad (17)$$

BOKHOVEN *et al.*¹⁾ assumed that the isotopic exchange between nitrogen and ammonia attained to its equilibrium at the outlet of the second portion of the catalyst, but we see from the comparison of z_i^A with z_i given in Table 2 that this is not the case. It follows that \bar{V}_e^{\rightarrow} is directly evaluated from the experimental result of the second portion.

The lower bound γ_L is now expressed according to (11.b) and (17), as

$$\gamma_L = \frac{(2n_e + a_e) \ln (z_{2,0}^N/z_{2,t}^N)}{a_e \ln [(z_i - z_0^A)/(z_i - z_t^A)]}. \quad (18)$$

It is not reasonable as shown below to calculate $\bar{V}_{1,e}^{\rightarrow}$ by substituting the value $z_{2,t}^N$ of z_2^N at the exchange equilibrium of (II) for $(z^{N(a)})^2$ in (10.a).

Denoting the concentration of N_2^0 *etc.* at the exchange equilibrium of (II) by $[N_2^0]$ *etc.*, we have, admitting the kinetic identity of nitrogen isotopes with BOKHOVEN *et al.*,¹⁾

$$[N_2^0]^2 = 4[N_2^0][N_2^0],$$

hence

$$z_{2,z}^N = [N_2^{30}]/([N_2^{30}] + [N_2^{29}] + [N_2^{28}]) = \{ [N_2^{30}]^{1/2} / ([N_2^{30}]^{1/2} + [N_2^{28}]^{1/2}) \}^2$$

$$= \{ [N_2^{30}]^{1/2} ([N_2^{30}]^{1/2} + [N_2^{28}]^{1/2}) / ([N_2^{30}]^{1/2} + [N_2^{28}]^{1/2})^2 \}^2$$

$$= \{ ([N_2^{30}] + [N_2^{28}]/2) / ([N_2^{30}] + [N_2^{29}] + [N_2^{28}]) \}^2 = (z^N)^2.$$

It follows that the above identification of $z_{2,z}^N$ with $(z^{N(a)})^2$ leads to the equation

$$z^N = z^{N(a)},$$

which holds according to (14), only when either $z^N = z^A$ or $\bar{V}_{1,e}^{\ddagger} \gg \bar{V}_{2,e}^{\ddagger}$. The former relation is negated as shown in Table 2. The latter is equivalent, with reference to (8. b), to premise a priori that one of the steps (2.I), (2.II) and (2.III) is the rate-determining step, *i. e.* what is just to be investigated.

TABLE 2. Calculation of r_L from the Experimental Results of BOKHOVEN *et al.*¹⁾

Runs	(1.2)*	(1.3)	(1.4)*	(2.2)	(2.3)	(2.4)
z_0^A %	0.532	0.573	0.536	0.675	0.661	0.671
z_1^A %	1.095	1.041	1.069	1.100	1.086	1.110
** z_t %	1.075	1.054	1.050	1.172	1.172	1.175
$z_{2,0}^N$ %	0.464	0.437	0.431	0.512	0.508	0.504
$z_{2,t}^N$ %	0.256	0.260	0.257	0.263	0.255	0.256
$z_{1,0}^N$ %	1.301	1.276	1.263	1.354	1.364	1.364
$z_{1,t}^N$ %	1.613	1.600	1.615	1.840	1.850	1.850
z_0^N %	1.115	1.075	1.063	1.189	1.190	1.186
z_t^N %	1.063	1.063	1.065	1.183	1.180	1.181
*** $(2n_e + a_e)/a_e$		23.1		24.1	24.1	24.1
r_L	—	3.3	—	8.3	9.4	8.0
** $r = \bar{\kappa} + 1$	—	3.8	—	9.2	10.2	8.7

*) Runs (1.2) and (1.4) are excluded, similarly as in the case of HORIUTI and TAKEZAWA¹⁶⁾, from the base of calculating r_L , because the thermodynamic requirement $z_t - z_t^A \geq 0$ is not fulfilled by the experimental data. In the latter cases the denominator of (17) hence r_L , is incomputable.

**) Calculated by HORIUTI and TAKEZAWA¹⁶⁾ from the experimental results of BOKHOVEN *et al.*¹⁾

***) The values at the outlet of the second portion of the catalyst.

****) This value is not accurate enough, inasmuch as the appropriate $(z_t - z_t^A)$ -value in (18) coincides nearly with the limit of error, *i. e.* 0.01% N¹⁵, stated by BOKHOVEN *et al.*¹⁾, of z^A or z^N -determination.

§ 3. Results and Conclusion

Table 2 shows the experimental results of BOKHOVEN *et al.*¹⁾ on the second portion of the catalyst and the values of γ_L calculated from them. The notations (1.2) *etc.* indicate the runs conducted with this portion after the designation of BOKHOVEN *et al.*¹⁾ The second last row of the Table shows the value of γ_L calculated from these results of respective runs according to (18). The last row shows γ for each run derived as follows. The ratio $\kappa \equiv \bar{V}_1/\bar{V}_2$ varies along with the progress of the reaction (1) during a run, where \bar{V}_1 or \bar{V}_2 is the unidirectional forward rate of (2.N) or the half of the unidirectional backward rate of NH_3 converting into $\text{N}(a)$. HORIUTI and one of the present authors¹⁶⁾ have evaluated the average $\bar{\kappa}$ of κ thus varying in the neighbourhood of the equilibrium of (1) for each run. Ignoring the deviation from the equilibrium of (1) in accordance with the present procedure, the average $\bar{\kappa}$ is identified with $\bar{V}_{1,e}/\bar{V}_{2,e}$ or with $\bar{V}_{1,e}/\bar{V}_{2,e}$. It follows, according to (8.a) and (9), that $\gamma = \bar{\kappa} + 1$, which determines the value of γ . We see from the comparison of the last two rows that the lower bound γ_L is appreciably close to the value of γ thus determined.

The present conclusion is that, even the value of γ_L being considerably greater than unity, (2.N) can not be the rate-determining step but one of the last three steps of (2), as follows from the argument in § 2.

It might be noted that the above conclusion has nothing to do with the questionable evaluation of k_s commented upon in § 1.

The present authors wish to express their sincere thanks to Professor J. HORIUTI, Dr. A. MATSUDA and Mr. G. TODA for their valuable discussion on the present work.

Summary

The conclusion of BOKHOVEN, GORGELS and MARS¹⁾ that the stoichiometric number $\nu(r)$ of the rate-determining step of the catalyzed synthesis of ammonia, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$, in the presence of doubly promoted iron catalyst was unity, was investigated. Their procedure of drawing the above conclusion from the observation of the rate of the synthesis and that of the associated exchange reaction, $\text{N}_2^{30} + \text{N}_2^{28} = 2\text{N}_2^{29}$, in the neighbourhood of the equilibrium of the synthesis was shown irrelevant because of the inadequate evaluation of the rate constant k_s of the synthesis used for the calculation of $\nu(r)$.

The analysis of the data of the above observations by BOKHOVEN *et al.*¹⁾, on the other hand, led, irrespective of k_s , to the conclusion that the rate-

determining step was not the dissociative adsorption of nitrogen molecule of the stoichiometric number 1, but one of the three steps of the common stoichiometric number 2, in which nitrogen atom picks up hydrogen atoms successively to complete ammonia. This conclusion contradicting that of BOKHOVEN *et al.*¹⁾ agrees with those arrived at previously by ENOMOTO, HORIUTI and KOBAYASHI^{8),9)}, HORIUTI and TOYOSHIMA^{14),15)} and HORIUTI and TAKEZAWA¹⁶⁾.

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