



Title	STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP AND THE MECHANISM OF CATALYZED AMMONIA SYNTHESIS IN THE PRESENCE OF COMMERCIAL IRON CATALYST
Author(s)	HORIUTI, Juro; TAKEZAWA, Nobutsune
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 8(2), 127-150
Issue Date	1960-10
Doc URL	http://hdl.handle.net/2115/24723
Type	bulletin (article)
File Information	8(2)_P127-150.pdf



[Instructions for use](#)

STOICHIOMETRIC NUMBER OF
THE RATE-DETERMINING STEP AND THE MECHANISM
OF CATALYZED AMMONIA SYNTHESIS IN
THE PRESENCE OF
COMMERCIAL IRON CATALYST

By

Juro HORIUTI and Nobutsune TAKEZAWA^{*)}

(Received June 30, 1960)

ENOMOTO, KOBAYASHI and one of the present authors¹⁾²⁾ have previously determined the stoichiometric number $\nu(r)$ of the rate-determining step r of the catalyzed ammonia synthesis



in the presence of doubly promoted iron catalyst at 2.

Let the synthesis (1) be the resultant of the set of steps



where (a) signifies the adsorbed state. Figures on the right give the numbers of times of the appropriate steps to occur for every act of the overall reaction (1), without afterall increasing or decreasing the intermediates, *i. e.* N(a), H(a), NH(a) and NH₂(a) in this case. These numbers are each the stoichiometric number of the appropriate step with regard to the overall reaction (1)³⁾⁻⁶⁾.

The above value 2 of $\nu(r)$ confines now the rate-determining step to one of the last three steps. On the basis of the above conclusion, TOYOSHIMA and one of the present authors⁷⁾ have shown that the first of the three, *i. e.* (2. III) is the rate-determining step by the statistical-mechanical analysis of the

^{*)} J. H.: Research Institute for Catalysis, Hokkaido University.
N. T.: Department of Chemistry, Faculty of Science, Hokkaido University.

decomposition rate of ammonia, and henceforth accounted for the hysteresis of the steady decomposition rate of ammonia, as observed by them⁸⁾, by allowing ammonia-hydrogen mixture to flow over the catalyst at 1 atm total pressure increasing stepwise the ammonia concentration in the mixture from one steady state of decomposition to the other successively and then decreasing reversely.

BOKHOVEN, GORGELS and MARS^{9)*} have recently determined $\nu(r)$ of the same reaction, finding that $\nu(r)=1$ in conformity with the rate-determining step of (2.I), contradicting the above conclusion⁷⁾.

The present paper is concerned with the examination of the latter paper with regard to the validity of their conclusion.

They observed the rate of synthesis and exchange of N^{15} simultaneously by allowing a mixture of nitrogen, hydrogen and ammonia not completely in equilibrium of (1) to flow through the catalyst's bed. The synthesis rate was hence observed at constant pressure rather than at constant volume and the exchange rate at incomplete equilibrium. They have calculated $\nu(r)$, however, by equations^{**)}, which are exact only when the rates of synthesis and of exchange implied are those observed respectively at constant volume and at perfect equilibrium of the synthesis^{***)}, by substituting for the latter, the rates of the synthesis and of exchange respectively observed at constant pressure and at incomplete equilibrium as mentioned above. The error of $\nu(r)$ introduced by these inexactitudes is not however very serious as shown in Appendix I.

The value of $\nu(r)$ by BOKHOVEN *et al.*⁹⁾ is, however, entirely distorted by the error in evaluation of the equilibrium concentration of ammonia as shown in §1. It is concluded in §2 that the value of $\nu(r)$ as given by them is, on account of this error, essentially the lower bound to the correct one.

A definite conclusion is deduced in §4, on the other hand, free from any uncertainty of the equilibrium concentration of ammonia mentioned above, from their simultaneous measurement on N_2^{30} , N_2^{29} and $N^{15}H_3$, that it is not (2.I) but one of the last three steps of (2), which determines the rate, in accordance with our previous conclusion¹⁾²⁾⁷⁾.

*) These authors (Ref. 9) refer the word "stoichiometric number" particularly to $\nu(r)$, *i. e.* the stoichiometric number of the rate-determining step. This terminology is irrelevant, since the concept of stoichiometric number is established for every constituent step of an overall reaction, whether it be rate-determining or not. Cf. §3.

***) They state that their equations for $\nu(r)$ are of different approach from that followed by HORIUTI and that these equations are equivalent to the corresponding ones used by HORIUTI. Exactly however, their equations are equivalent to ours derived for constant volume (Ref. 10, 11) but not those for constant pressure (Ref. 10, 11) relevant to their experimental condition; their equations are hence, besides being appropriate to the exchange rate at complete equilibrium of (1), irrelevant to their experimental condition.

****) Cf. Appendix I.

§ 1. Sensitivity of $\nu(r)$ to the Equilibrium Concentration of Ammonia.

According to the paper of BOKHOVEN *et al.*⁹⁾, the value of $\nu(r)$ is given in terms of observable quantities, as*):

$$\nu(r) = \frac{4/P_e^A + 1/P_e^N + 9/P_e^H}{2/P_e^A + 1/P_e^N} \cdot \frac{\log(z_0^A - z_i)/(z_i^A - z_i)}{\log(x_e^A - x_0^A)/(x_e^A - x_i^A)}, \quad (3)$$

where P_e^A , P_e^N and P_e^H are partial pressures of ammonia, nitrogen and hydrogen at equilibrium of (1), z_0^A , z_i^A and z_i the atomic fraction of N¹⁵ in ammonia respectively at the beginning of the contact with the catalyst, at its end and at the exchange equilibrium, and x_0^A , x_i^A and x_e^A the mol fractions of ammonia in the gas mixture respectively at the beginning of the contact with the catalyst, at the end and at the equilibrium of (1).

It is important that $\nu(r)$ decreases rapidly with decrease of x_e^A according to (3) for the experimental condition of BOKHOVEN *et al.*⁹⁾, where x_i^A is very close to x_e^A , i.e. x_i^A/x_e^A or η (outlet), as denoted by BOKHOVEN *et al.*⁹⁾, ranges from 0.958 to 0.996 in their first series of experiments conducted at 429°C and 7.5 atm total pressure or from 0.876⁶ to 0.937⁷ in their second series at 425°C and the same total pressure. The relative decrease of $x_e^A - x_i^A$ due to the numerical decrement of x_e^A is greater than that of $x_e^A - x_0^A$, inasmuch as $x_i^A > x_0^A$

*) This equation reproduces the procedure of calculation of $\nu(r)$ by BOKHOVEN *et al.* as shown below. The $\nu(r)$ is expressed by Eq.(7) of their paper (Ref. 9) as

$$\nu(r) = \frac{\bar{n}_s}{k_s} \left(\frac{4}{P_e^A} + \frac{1}{P_e^N} + \frac{9}{P_e^H} \right),$$

where notations $1/a$, $P_{NH_3(eq)}$, $P_{N_2(eq)}$ and $P_{H_2(eq)}$ used by them are replaced respectively by $\nu(r)$, P_e^A , P_e^N and P_e^H . The k_s in the above equation is given by its expression in Table 1 of their paper with reference to those of η (inlet) and η (outlet) given there; replacing the notations NH₃(inlet), NH₃(outlet) and NH₃(eq) in the resulting expression of k_s respectively by x_0^A , x_i^A and x_e^A , we have

$$k_s = V_s \ln \frac{x_e^A - x_0^A}{x_e^A - x_i^A},$$

where V_s is the space velocity. Eq.(9) in their paper (Ref. 9) is written on the other hand by replacing the contact time t with the reciprocal of V_s , and P_{NH_3} and P_{N_2} there (the latter two must be identical with $P_{NH_3(eq)}$ and $P_{N_2(eq)}$ in Eq. (7) of their paper) by P_e^A and P_e^N , and z_0 , z and z_{eq} by z_0^A , z_i^A and z_i , as

$$\bar{n}_{e,I}(2/P_e^A + 1/P_e^N) = V_s \ln [(z_0^A - z_i)/(z_i^A - z_i)].$$

Eq.(3) in the text is obtained by eliminating k_s and \bar{n}_s , equated to $\bar{n}_{e,I}$ as stated in their paper, from the above three equations.

or in other words the equilibrium of (1) is approached exclusively by synthesis in their experiments. It follows that $\log(x_e^A - x_0^A)/(x_e^A - x_t^A)$ in the denominator of (3) increases appreciably with decrease of x_e^A . The first factor of (3) is much less sensitive to x_e^A , as seen from the transcription $2(1+3x_e^A)/(1+x_e^A)$ of the factor according to the relation $P_e^A : P_e^N : P_e^H = x_e^A : \frac{1}{4}(1-x_e^A) : \frac{3}{4}(1-x_e^A)$ for the 1:3 nitrogen-hydrogen ratio and the value of x_e^A near 0.02 in their experiments. The $\nu(r)$ -value increases in consequence considerably with increase of x_e^A as shown in Table 1 and 2.

Each column of Table 1 and 2 shows the value of $100x_e^A$ used by BOKHOVEN *et al.*⁹⁾, $\nu(r)$ calculated from the latter and that from $100x_e^A=2.36$ for each run. This value 2.36 of $100x_e^A$ was taken slightly above the uppermost value 2.34 just to see the sensitivity in question in this case, too.

TABLE 1. Sensitivity of $\nu(r)$ to x_e^A .
First series experiment of BOKHOVEN *et al.*⁹⁾

$100x_e^A$ by BOKHOVEN <i>et al.</i> ^{9)*)}		2.15	2.18	2.215	2.26	2.34
$\nu(r)$ calculated	$100x_e^A$ given above	1.15	1.22	0.82	0.95	0.83
by (3) from	$100x_e^A=2.36$	2.7	5.6	5.1	1.7	1.5

*) Calculated back from $\text{NH}_3(\text{inlet})$ and $\vartheta(\text{inlet})$ as given by BOKHOVEN *et al.* (Ref. 9) as $100x_e^A = \text{NH}_3(\text{inlet}) / \vartheta(\text{inlet})$.

TABLE 2. Sensitivity of $\nu(r)$ to x_e^A .
Second series experiment of BOKHOVEN *et al.*⁹⁾

$100x_e^A$ given directly by BOKHOVEN <i>et al.</i> ⁹⁾		2.194	2.212	2.192	2.114	2.119	2.120
$\nu(r)$ calculated	$100x_e^A$ given above	1.10	1.57	1.13	1.01	0.90	1.19
by (3) from	$100x_e^A=2.36$	1.67	2.23	1.70	2.09	1.89	2.37

We see from the latter case that $\nu(r)$ is almost doubled by increasing $100x_e^A$ from 2.34 to 2.36 *i.e.* only by less than 1%, hence that x_e^A must be accurate within 0.1% for a reasonable evaluation of $\nu(r)$. The $\nu(r)$ of other runs in Table 1 is extravagantly raised by replacing $100x_e^A$ -values given by them with 2.36, which nearly equals 2.34 observed by them at the same temperature and total pressure. The $\nu(r)$ in the second series must be greater than the value given in the last row of Table 2, provided that 2.36 corresponds to the equilibrium concentration at 429°C of the first series, since it must yet be higher at 425°C of the second series.

The reliability of $\nu(r)$ given by these authors depends thus first of all on

that of x_e^A , which is investigated in the next section.

§ 2. Investigation of the Reliability of x_e^A -Data

BOKHOVEN *et al.*⁹⁾ have identified x_e^A observed at low space velocity with x_e^A for each run. Let us assume that x_e^A thus determined corresponds to the thermodynamical equilibrium. The fluctuation of x_e^A should then depend on those of temperature and pressure, which amounts to *ca.* 2% of its value as shown below on the basis of their experimental condition.

The equilibrium constant K of (1) is expressed in terms of the total pressure P_T , the ratio λ of hydrogen to nitrogen and x_e^A as

$$K = \frac{P_T^2 (x_e^A)^2}{\{\lambda P_T (1 - x_e^A)/(1 + \lambda)\}^2 P_T (1 - x_e^A)/(1 + \lambda)},$$

which gives on logarithmic differentiation

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

The third term in the parentheses in the above equation vanishes for the present cases in question when $\lambda=3$, so that the relative error μ^v of x_e^A is expressed in terms of those μ^K and μ^P of K and P_T as

$$\mu^v = \frac{1 - x_e^A}{1 + x_e^A} \left[(\mu^K/2)^2 + (\mu^P)^2 \right]^{1/2}.$$

BOKHOVEN *et al.*⁹⁾ state that the temperature of a fluidized bed of carborundum powder, which surrounds the catalyst's bed, was kept within 1°C. The temperature of the catalyst may be admitted to have been kept constant within the same range, inasmuch as the minute amount of ammonia synthesis during the contact would hardly disturb the temperature. The $\mu^K/2$ for the fluctuation of 1°C is calculated at 0.0130 according to the HABER's formula for K (Ref. 12) *i. e.*

$$\frac{1}{2} \log K = \frac{9591}{4.571 T} - \frac{4.98}{1.985} \log T - \frac{4.6 \times 10^{-4}}{4.571} T + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10.$$

No description is found in their paper as to the constancy of the total pressure, but we might assume safely on the basis of the usual performance of the pressure gauge, that the total pressure was kept within 0.1 atm, or μ^P is 0.0133 for the total pressure of 7.5 atm.

The μ^v is now 0.0179 according to the second last equation.

It is now questionable, how the accuracy of 0.1%*⁹⁾ was secured under the above experimental condition. We would not, however, go into this question but compare the above conclusion with their result.

We see from Table 1, that $100x_e^A$ given by them⁹⁾ for the first series fluctuates by *ca.* 9%. The $100x_e^A$ of the second series of their experiment, when reduced

*) Cf. § 1.

from the temperature 425°C of the series to that 429°C of the first series, are*)

2.09 2.10 2.09 2.01 2.02 2.02 .

Incorporating the above values with those of Table 1, the fluctuation of x_e^A given by them⁹⁾ amounts to 15%, which far exceeds *ca.* 2% deduced from the presupposition that their x_e^A corresponds to the thermodynamical equilibrium.

The latter presupposition must in consequence be negatived. The x_e^A given by them must hence be either appreciably greater or less than that at the thermodynamical equilibrium. It is, however, thermodynamically impossible for the mol fraction of ammonia x^A to exceed the true value of x_e^A , when approached exclusively by synthesis as in the case of their experiment. The x_e^A given by them must in consequence be appreciably lower than the thermodynamical value. Since $\nu(r)$ decreases with decrease of x_e^A as shown in §1, $\nu(r)$ given by them is actually a lower bound to the true value. Their result is in consequence consistent with ours, *i. e.* $\nu(r)=2$, which was based, in contrast to their case, on the value of x_e^A located by approaching it both by synthesis and decomposition at the very condition of the experiment.

§ 3. Investigation of the Rate-Determining Step

A definite conclusion on the rate-determining step is deduced, besides that drawn in the foregoing section, from their observation on the variation of contents of N_2^{30} , N_2^{29} and $N^{15}H_3$ through the contact with the catalyst as below, without being troubled by the uncertainty of x_e^A dealt with above. The method of analysis is outlined in this section and applied to the above data in the next section.

BOKHOVEN *et al.*⁹⁾ base, as we do, their method of $\nu(r)$ -determination on the postulates: (a) that the isotopic exchange is effected exclusively through the steps which give rise to the synthesis reaction, (b) that the steady state is established with respect to every intermediate and (c) that there exists practically no isotopic difference of rates of any step. The postulate (a) is explicitly stated in their paper, whereas (b) and (c) must be taken tacitly assumed, insofar as they are major premises to the existence of the rate-determining step and to the isotopic determination of the unidirectional rate.

We will base the following argument on the same set of postulates but

*) The K decreases by 10.4% with increase of temperature from 425°C to 429°C according to the HABER's formula (Ref.12) quoted on p. 3. The corresponding decrease of x_e^A is calculated at 5.0% for $x_e^A=0.02$ according to the above expression of K . These x_e^A -values are given by decreasing those in the first row of Table 2 by 5.0%.

discriminate between the forward and the backward rates of every step involved in order to allow for the equilibrium of (1) incompletely established in the case of their experiment.

At the steady state of a reaction, we have

$$V = [\bar{v}(s) - \bar{v}(s)] / \nu(s), \quad s = 1, \dots, S, \quad (4)$$

where $\bar{v}(s)$ or $\bar{v}(s)$ is the forward or backward rate of the constituent step s of the overall reaction and $\nu(s)$ its stoichiometric number in the particular case of a single reaction route, *i.e.* when there exists a single mode of assigning the stoichiometric numbers to the constituent steps as in the case of (2) to compose the overall reaction (1)⁵⁾.

The number P of reaction routes or of independent modes of assigning the stoichiometric numbers equals the total number S of steps minus the number I of independent intermediates implied in the steps, *i.e.*⁵⁾

$$P = S - I.$$

The I is the number of such intermediates as their increments, each given by a linear homogeneous function of numbers of acts of steps, are linearly independent and the increment of every other intermediate is given as a linear combination of them. An alternative definition of I is the rank of the matrix $(b_{i,s})$ of the number $b_{i,s}$ of i '-th intermediate formed by s -th step, where i ' numbers all intermediates involved in the set of S steps. In the case of (2), the intermediates are N(a) , H(a) , NH(a) and $\text{NH}_2(\text{a})$, *i.e.* $I=4$, which happens to equal I , while $S=5$, so that $P=S-I=5-4=1$.

In the latter particular case, there may exist a rate-determining step r , defined such a step among s 's as

$$\bar{v}(r)/\nu(r), \bar{v}(r)/\nu(r) \ll \bar{v}(s)/\nu(s), \bar{v}(s)/\nu(s), \quad s \neq r \quad (5)$$

at the steady state, so that

(A) $\nu(r)$ -times the occurrence of r in the forward or backward direction is sufficient once to complete the overall reaction in the same direction, being accompanied by (5) practically with certainty with each $\nu(s)$ -times the forward or backward acts of every other step than r and

$$(B) \quad \bar{v}(s) \doteq \bar{v}(s), \quad s \neq r \quad (6)$$

according to (4) and (5).

For any overall reaction of a single route, however, it is necessary for r to occur $\nu(r)$ -times for every act of the overall reaction⁵⁾. The $\nu(r)$ -times occurrence of r in either direction is thus necessary as well as sufficient for one act of the overall reaction in that direction, hence

$$\bar{V} = \bar{v}(r)/\nu(r), \quad \bar{V} = \bar{v}(r)/\nu(r), \quad (7. a), (7. b)$$

where \vec{V} or \overleftarrow{V} is the forward or backward unidirectional rate of the overall reaction. It follows from (4) and (7), that

$$V = \vec{V} - \overleftarrow{V}. \quad (8)$$

We define now \vec{V}_1 and \overleftarrow{V}_1 as

$$\vec{V}_1 = \bar{v}(I)/\nu(I), \quad \overleftarrow{V}_1 = \bar{v}(I)/\nu(I), \quad (9. a), (9. b)$$

\vec{V}_{III} , \overleftarrow{V}_{III} etc. as

$$\vec{V}_\chi = \bar{v}(\chi)/\nu(\chi), \quad \overleftarrow{V}_\chi = \bar{v}(\chi)/\nu(\chi), \quad \chi = III, IV, V \quad (10. a), (10. b)$$

and \vec{V}_2 or \overleftarrow{V}_2 as the half the unidirectional rate of N(a) converted into NH₃ or of NH₃ reversely into N(a) respectively, where I etc. denote steps (2.I) etc. respectively*). It follows from the above definitions that

$$\frac{1}{\vec{V}_2} = \frac{1}{\vec{V}_{III}} + \frac{1}{\overleftarrow{V}_{IV}} \frac{\vec{V}_{III}}{\vec{V}_{III}} + \frac{1}{\overleftarrow{V}_V} \frac{\vec{V}_{III}}{\vec{V}_{III}} \frac{\overleftarrow{V}_{IV}}{\overleftarrow{V}_{IV}}, \quad (11. a)$$

$$\frac{1}{\overleftarrow{V}_2} = \frac{1}{\overleftarrow{V}_V} + \frac{1}{\overleftarrow{V}_{IV}} \frac{\overleftarrow{V}_V}{\overleftarrow{V}_V} + \frac{1}{\vec{V}_{III}} \frac{\overleftarrow{V}_V}{\overleftarrow{V}_V} \frac{\overleftarrow{V}_{IV}}{\overleftarrow{V}_{IV}}. \quad (11. b)$$

Eq.(11.a) is derived as follows. N(a) is transferred to NH(a) at a rate $2\vec{V}_{III}$ and NH(a) thus formed converts forwards into NH₂(a) or backwards into N(a) respectively at a rate $2\vec{V}_{III}$ or $2\overleftarrow{V}_{IV}$; the rate of N(a) converting straightforward into NH₂(a) is thus $2f_{IV}\vec{V}_{III}$, where $f_{IV} = \vec{V}_{IV}/(\vec{V}_{III} + \overleftarrow{V}_{IV})$. The NH₂(a) thus formed converts further forwards into NH₃ to complete the full course of N(a) transforming into NH₃ or backwards into NH(a) respectively at a rate $2\vec{V}_V$ or $2\overleftarrow{V}_{IV}$. The rate of N(a) converting straightforward into NH₃ is now $2f_{IV}f_V\vec{V}_{III}$, where $f_V = \vec{V}_V/(\vec{V}_{IV} + \overleftarrow{V}_V)$.

The unidirectional rate of change of N(a) into NH₃ should include, besides the rate of the above straightforward transformation, those of such transits as NH₂(a) once formed returns back to NH(a) n times before entering the final step (2.V) to complete the transformation from N(a) to NH₃. The rate of the latter transit is $2f_{IV}f_V\vec{V}_{III}f_{IV}^n(1-f_V)^n$, which includes the above rate $2f_{IV}f_V\vec{V}_{III}$ of the straightforward conversion as its special case, when $n=0$.

The total unidirectional rate $2\vec{V}_2$ of N(a) converting into NH₃ is thus given by the total sum of $2f_{IV}^{n+1}f_V(1-f_V)^n\vec{V}_{III}$ for all n -values from zero to infinity, i.e. as $2\vec{V}_2 = 2\sum_{n=0}^{\infty} f_{IV}^{n+1}f_V(1-f_V)^n\vec{V}_{III}$ or $2\vec{V}_2 = 2\vec{V}_{III}f_{IV}f_V/(1-f_{IV}+f_{IV}f_V)$, which leads to (11.a) by expressing f_{IV} and f_V as defined above.

Eq. (11.b) is derived by following the above procedure reversely or formally by permuting III and V and reversing the arrows.

It follows from (5), (6), (7), (9) and (10), that, if (2.I) determines the rate, both \vec{V}_1 and \overleftarrow{V}_1 are sufficiently small compared with any of \vec{V}_χ and \overleftarrow{V}_χ , and

*) The unidirectional rate of N(a)'s converted into NH₃ is that with which N(a)'s complete the whole course of the conversion without returning to the start, i.e. the state of N(a).

Stoichiometric Number of the Rate-Determining Step

that $\vec{V}_z \doteq \vec{V}_z$, hence according to (11. b) that

$$\kappa \equiv \vec{V}_1/\vec{V}_2 \ll 1. \quad (12. a)$$

If alternatively one of χ 's is the rate-determining step, \vec{V}_2 practically equals the appropriate \vec{V}_z according to (5), (6), (10) and (11. b), hence by (5), (9) and (10), it is sufficiently smaller than \vec{V}_1 , *i. e.*

$$\kappa \equiv \vec{V}_1/\vec{V}_2 \gg 1. \quad (12. b)$$

The rate-determining step may in consequence be determined by deciding the value of κ from the observation of BOKHOVEN *et al.*⁹⁾ as in the next section.

§ 4. Determination of the rate-determining step

Consider a definite portion of the gas mixture conveyed through the catalyst's bed by a piston flow. The rate of increase of N_2^{30} or N_2^{29} in the definite portion is expressed as

$$d(nz_2^N)/dt = -\vec{V}_1 z_2^N + \vec{V}_1 (z^{N(a)})^2 \quad (13. a)$$

or*)

$$d(nz_2^N)/dt = -\vec{V}_1 z_1^N + 2\vec{V}_1 z^{N(a)}(1 - z^{N(a)}), \quad (13. b)$$

where n is the total number of mols of nitrogen in the definite portion of gas mixture, z_2^N or z_1^N the mol fraction of N_2^{30} or N_2^{29} there, $z^{N(a)}$ the atomic fraction of N^{15} in $N(a)$ and t the time of contact with the catalyst.

Steady condition is given for $N(a)$ as a whole or for $N^{15}(a)$ in particular respectively as

$$\vec{V}_1 - \vec{V}_1 = \vec{V}_2 - \vec{V}_2, \quad (14. a)$$

$$\vec{V}_1(2z_2^N + z_1^N) - 2\vec{V}_1 z^{N(a)} = 2\vec{V}_2 z^{N(a)} - 2\vec{V}_2 z^A, \quad (14. b)$$

where z^A is the fraction of $N^{15}H_3$ over whole gaseous ammonia. The steady condition leads necessarily to the conservation of the total amount n^{15} of N^{15} contained in the definite portion of the gas mixture, as

$$n(2z_2^N + z_1^N) + az^A = n^{15}, \quad (15)$$

*) The unidirectional rate of formation of N_2^{29} from $N(a)$'s is given, according to the postulate (c), §3, by the overall unidirectional rate \vec{V}_1 of nitrogen formation multiplied by the fraction of the combination of $N^{14}(a)$ and $N^{15}(a)$ over the overall combination of two $N(a)$'s. Let $n^{14}(a)$ and $n^{15}(a)$ be the number of $N^{14}(a)$ and $N^{15}(a)$ existing. The combination of $N^{14}(a)$ and $N^{15}(a)$ is $n^{14}(a)n^{15}(a)$, while the overall combination of two $N(a)$'s is $(n^{14}(a) + n^{15}(a))(n^{14}(a) + n^{15}(a) - 1)/2!$ or practically $(n^{14}(a) + n^{15}(a))^2/2$. The fraction in question is now given as $2z^{N(a)}(1 - z^{N(a)})$, hence the rate of supply of N_2^{29} in question is given by the second term on the right of (13. b).

where a is the number of mols of ammonia in that portion.

We have now by eliminating $\bar{V}_1 + \bar{V}_2$ from (14.a) and (14.b),

$$z^{N(a)} = (\kappa z^N + z^A)/(\kappa + 1), \quad (16. a)$$

where

$$z^N = z_2^N + z_1^N/2 \quad (16. b)$$

and

$$\kappa \equiv \bar{V}_1/\bar{V}_2. \quad (16. c)$$

It follows on the other hand from the definitions of n , \bar{V}_1 and \bar{V}_2 that

$$dn/dt = \bar{V}_2 - \bar{V}_1.$$

Eqs. (13.a) and (13.b) are reduced, eliminating \bar{V}_2 from them and the above equation, to the forms

$$-n \frac{dz_2^N}{dt} = \bar{V}_1 \{ z_2^N - (z^{N(a)})^2 \} \quad (17. a)$$

and

$$-n \frac{dz_1^N}{dt} = \bar{V}_1 \{ z_1^N - 2z^{N(a)}(1 - z^{N(a)}) \}. \quad (17. b)$$

Adding (17.b) to two times (17.a), we have, referring to (16.b)

$$-n dz^N/dt = \bar{V}_1 (z^N - z^{N(a)})$$

or substituting $z^{N(a)}$ from (16.a)

$$n \frac{dz^N}{dt} = \bar{V}_1 \frac{z^A - z^N}{\kappa + 1} \quad (18)$$

Eqs.(15) and (16.b) give on the other hand

$$2nz^N + az^A = n^{15}. \quad (19)$$

The above two equations give on elimination of z^A from them

$$n \frac{dz^N}{dt} = \bar{V}_1 \alpha (z_i - z^N)/(\kappa + 1), \quad (20. a)$$

where

$$\alpha = (2n + a)/a, \quad z_i = n^{15}/(2n + a). \quad (20. b), (20. c)$$

The z_i is the fraction of the total number of N^{15} atoms over the whole nitrogen atoms comprised in the definite portion of the gas mixture or, according to the postulate (c), §3, the common value attained both by z^N and z^A at the exchange equilibrium between nitrogen and ammonia.

Eq.(20.a) is now integrated as

$$z^N - z_i = (z_0^N - z_i) \exp(-\bar{k}_1 t), \quad (21. a)$$

where

$$\bar{k}_1 = \frac{1}{t} \int_0^t \frac{\bar{V}_1}{n} \frac{\alpha}{1+\kappa} dt \quad (21. b)$$

and z_0^N is the value of z^N at $t=0$. Eliminating z^N , z^A and n^{15} from (16.a), (19), (20.c) and (21.a), we have

$$z^{N(a)} = \left\{ 1 - \frac{2n+a}{a(1+\kappa)} \right\} (z_0^N - z_i) \exp(-\bar{k}_1 t) + z_i$$

or with reference to (20.b)

$$z^{N(a)} = \left(1 - \frac{\alpha}{1+\kappa} \right) (z_0^N - z_i) \exp(-\bar{k}_1 t) + z_i. \quad (22)$$

The $z^{N(a)}$ and in consequence the second term in the parentheses of (17.a) or (17.b) are thus given as functions of time. These equations are integrated as

$$z_2^N = e^{-\bar{k}_2 t} \left\{ \int_0^t e^{\bar{k}_2 t} \frac{\bar{V}_1}{n} (z^{N(a)})^2 dt + z_{2,0}^N \right\}, \quad (23. a)$$

$$z_1^N = e^{-\bar{k}_2 t} \left\{ \int_0^t e^{\bar{k}_2 t} \frac{\bar{V}_1}{n} \cdot 2z^{N(a)}(1 - z^{N(a)}) dt + z_{1,0}^N \right\}, \quad (23. b)$$

where

$$\bar{k}_2 = \frac{1}{t} \int_0^t \frac{\bar{V}_1}{n} dt \quad (23. c)$$

and $z_{2,0}^N$ or $z_{1,0}^N$ is the value of z_2^N or z_1^N at $t=0$ respectively.

Substituting $z^{N(a)}$ from (22) into (23) and carrying out the integration regarding both \bar{k}_1 and \bar{k}_2 constant, we have

$$z_2^N = z_{2,0}^N e^{-\bar{k}_2 t} + z_i^2 (1 - e^{-\bar{k}_2 t}) + \varepsilon_2, \quad (24. a)$$

$$z_1^N = z_{1,0}^N e^{-\bar{k}_2 t} + 2z_i (1 - z_i) (1 - e^{-\bar{k}_2 t}) + \varepsilon_1, \quad (24. b)$$

where

$$\begin{aligned} \varepsilon_2 &= 2(z_0^N - z_i) z_i e^{-\bar{k}_2 t} \int_0^t \frac{\bar{V}_1}{n} \left(1 - \frac{\alpha}{1+\kappa} \right) e^{(\bar{k}_2 - \bar{k}_1) t} dt \\ &\quad + (z_0^N - z_i)^2 e^{-\bar{k}_2 t} \int_0^t \frac{\bar{V}_1}{n} \left(1 - \frac{\alpha}{1+\kappa} \right)^2 e^{(\bar{k}_2 - 2\bar{k}_1) t} dt, \end{aligned} \quad (25. a)$$

$$\begin{aligned} \varepsilon_1 = & 2(z_0^N - z_i)(1 - 2z_i)e^{-\bar{k}_2 t} \int_0^t \frac{\bar{V}_1}{n} \left(1 - \frac{\alpha}{1 + \kappa}\right) e^{(\bar{k}_2 - \bar{k}_1)t} dt \\ & - 2(z_0^N - z_i)^2 e^{-\bar{k}_2 t} \int_0^t \frac{\bar{V}_1}{n} \left(1 - \frac{\alpha}{1 + \kappa}\right)^2 e^{(\bar{k}_2 - 2\bar{k}_1)t} dt. \end{aligned} \quad (25. b)$$

Eqs.(24) and (25) are further transformed as follows for the sake of the numerical calculation. The ratio \bar{k}_1/\bar{k}_2 is given by (21. b) and (23. c) as

$$\frac{\bar{k}_1}{\bar{k}_2} = \int_0^t \frac{\alpha}{1 + \kappa} \frac{\bar{V}_1}{n} dt \bigg/ \int_0^t \frac{\bar{V}_1}{n} dt$$

or the average of $\alpha/(1 + \kappa)$ over $(\bar{V}_1/n)dt$, which may be identified with $\bar{\alpha}/(1 + \bar{\kappa})$, where $\bar{\alpha}$ or $\bar{\kappa}$ is a simple average $(1/t) \int_0^t \alpha dt$ or $(1/t) \int_0^t \kappa dt$ over the time of contact, admitting only slight variations of α , κ and \bar{V}_1/n during the contact, as

$$\bar{k}_2/\bar{k}_1 = (1 + \bar{\kappa})/\bar{\alpha}.$$

Hence we have according to (21. a)

$$\exp(-\bar{k}_2 t) = Z^{(1 + \bar{\kappa})/\bar{\alpha}}, \quad (26. a)$$

where

$$Z = (z^N - z_i)/(z_0^N - z_i) \quad (26. b)$$

or

$$Z = \exp(-\bar{k}_1 t). \quad (26. c)$$

Eq.(24) is now written according to (26. a) in the form

$$1 + \bar{\kappa} = \frac{\bar{\alpha} \log [(z_{2,t}^N - z_i^2 - \varepsilon_2)/(z_{2,0}^N - z_i^2)]}{\log Z} \quad (27. a)$$

$$1 + \bar{\kappa} = \frac{\bar{\alpha} \log [\{z_{1,t}^N - 2z_i(1 - z_i) - \varepsilon_1\}/\{z_{1,0}^N - 2z_i(1 - z_i)\}]}{\log Z}, \quad (27. b)$$

where $z_{2,t}^N$ or $z_{1,t}^N$ is the value of z_2^N or z_1^N at the end of the contact time t . Eq.(25) is transformed identifying $\alpha/(1 + \kappa)$ in the integration with $\bar{\alpha}/(1 + \bar{\kappa})$ and \bar{V}_1/n with its mean value \bar{k}_2 according to (23. c), as

$$\begin{aligned} \varepsilon_2 = & (z_0^N - z_i) \left(1 - \frac{\bar{\alpha}}{1 + \bar{\kappa}}\right) \left[\frac{2z_i \bar{k}_2}{\bar{k}_2 - \bar{k}_1} (e^{-\bar{k}_1 t} - e^{-\bar{k}_2 t}) \right. \\ & \left. + (z_0^N - z_i) \left(1 - \frac{\bar{\alpha}}{1 + \bar{\kappa}}\right) \frac{\bar{k}_2}{\bar{k}_2 - 2\bar{k}_1} (e^{-2\bar{k}_1 t} - e^{-\bar{k}_2 t}) \right], \end{aligned}$$

$$\begin{aligned} \varepsilon_1 = & 2(z_0^N - z_i) \left(1 - \frac{\bar{\alpha}}{1 + \bar{\kappa}}\right) \left[\frac{(1 - 2z_i) \bar{k}_2}{\bar{k}_2 - \bar{k}_1} (e^{-\bar{k}_1 t} - e^{-\bar{k}_2 t}) \right. \\ & \left. - (z_0^N - z_i) \left(1 - \frac{\bar{\alpha}}{1 + \bar{\kappa}}\right) \frac{\bar{k}_2}{\bar{k}_2 - 2\bar{k}_1} (e^{-2\bar{k}_1 t} - e^{-\bar{k}_2 t}) \right] \end{aligned}$$

or expressing $\exp(-\bar{k}_1 t)$, $\exp(-\bar{k}_2 t)$, $\bar{k}_2/(\bar{k}_2 - \bar{k}_1)$ and $\bar{k}_2/(\bar{k}_2 - 2\bar{k}_1)$ in terms of $\bar{\alpha}$, \bar{k} and Z by (26.a) and (26.c), as

$$\varepsilon_2 = (z_0^N - z_i) \left[2z_i(Z - Z^{(1+\bar{k})/\bar{\alpha}}) + \frac{(z_0^N - z_i)(1 + \bar{k} - \bar{\alpha})^2}{(1 + \bar{k})(1 + \bar{k} - 2\bar{\alpha})} (Z^2 - Z^{(1+\bar{k})/\bar{\alpha}}) \right], \quad (28. a)$$

$$\varepsilon_1 = 2(z_0^N - z_i) \left[(1 - 2z_i)(Z - Z^{(1+\bar{k})/\bar{\alpha}}) - \frac{(z_0^N - z_i)(1 + \bar{k} - \bar{\alpha})^2}{(1 + \bar{k})(1 + \bar{k} - 2\bar{\alpha})} (Z^2 - Z^{(1+\bar{k})/\bar{\alpha}}) \right]. \quad (28. b)$$

The \bar{k} was now determined by (27) from the observation of BOKHOVEN *et al.*⁹⁾ first ignoring ε_2 or ε_1 anticipating that it is sufficiently small because of the factor $z_0^N - z_i$ comprised in its expression (28), which is subsequently verified by substituting the value of \bar{k} thus obtained into (28) to calculate ε_2 or ε_1 . The value of ε_2 or ε_1 thus obtained was now substituted into (27) to work out \bar{k} again; the successive approximation was thus followed until the significant figures of \bar{k} was no more changed by proceeding with it.

The Z was numerically calculated by the equation,

$$Z = (z_i - z^A)/(z_i - z_0^A), \quad (29)$$

which is formally identical with (26.b) according to the equation

$$2n(z^N - z_i) = a(z_i - z^A) \quad (30)$$

derived readily from (19) and (20.c), since $z_i - z_0^A$ or $z_i - z_i^A$ must be $2n/a \doteq 25$ times as large as $z_0^N - z_i$ or $z_i^N - z_i$ respectively according to (30), hence the relative error of the former or that of Z calculated by (29) so much smaller.

The z_i was taken the mean of its values at the "inlet", "middle" and "outlet" of the second series experiment of BOKHOVEN *et al.*⁹⁾ respectively worked out by the equation

$$z_i = \frac{2n/a \cdot (z_2^N + z_1^N/2) + z^A}{2n/a + 1}, \quad (31)$$

which follows from (15) and (20.c). The n/a in (31) was calculated by the equation

$$n/a = (1 - x^A)/4x^A, \quad (32)$$

where x^A is the mol fraction of ammonia given by BOKHOVEN *et al.*⁹⁾ at the respective point.

Table 3 shows the values of z_i at these points and their mean for each run denoted after these authors⁹⁾.

It is neither sound nor necessary as seen above to assume z^A at the "outlet" arbitrarily to be z_i as did by the latter authors⁹⁾. Results of runs 1.2 and

TABLE 3. $100z_i$ -values from the second series experiment of BOKHOVEN *et al.*⁹⁾

Runs	1.2	1.3	1.4	2.2	2.3	2.4
"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	1.054	1.050	1.172	1.172	1.175

1.4 are omitted from the further treatment for $\bar{\kappa}$, inasmuch as the mean value of $100z_i$ *i.e.* 1.075 or 1.050 given in the above Table is exceeded by $100z_i^A$ at the "outlet", *i.e.* 1.095 or 1.069 in the respective case, which is thermodynamically absurd on the basis of the postulate (c), §3*).

The $\bar{\kappa}$ is now worked out from other runs as shown in Table 4 attributing $z_{1,0}^N$ or $z_{2,0}^N$ and $z_{1,t}^N$ or $z_{2,t}^N$ to those at the "middle" and the "outlet" respectively.

TABLE 4. Calculation of the mean value $\bar{\kappa}$ of $\kappa \equiv \vec{V}_1/\vec{V}_2$ from the second series experiments of BOKHOVEN *et al.*⁹⁾

No of runs	1.3	2.2	2.3	2.4
$\bar{\alpha}$	24.7	25.0	24.9	25.1
$1/Z$	37.0	6.90	5.94	7.76
$100(z_{2,0}^N - z_2^2)$	0.426	0.498	0.494	0.490
$100(z_{2,t}^N - z_2^2)$	0.249	0.249	0.241	0.242
$100\varepsilon_2$	-2.4×10^{-4}	-1.4×10^{-4}	-1.3×10^{-4}	-0.93×10^{-4}
$100\{z_{1,0}^N - 2z_1(1 - z_1)\}$	-0.806	-0.962	-0.952	-0.956
$100\{z_{1,t}^N - 2z_1(1 - z_1)\}$	-0.482	-0.476	-0.466	-0.470
$100\varepsilon_1$	-0.024	-0.012	-0.011	-0.008
$\bar{\kappa}$ from $\begin{cases} z_2^N & \text{by (28. a) and (27. a)} \\ z_1^N & \text{by (28. b) and (27. b)} \end{cases}$	2.7	8.0	9.0	7.7
	2.8	8.4	9.3	7.9

The $\bar{\alpha}$ shown in the second row is the mean of the values of α at the "middle" and the "outlet" calculated by (20. b) and (32). The fourth and fifth rows of the Table show the values of $z_{2,0}^N - z_2^2$ and $z_{2,t}^N - z_2^2$ in (27. a), derived from the experimental results of BOKHOVEN *et al.*

*) The z_i -values at the three points "inlet", "middle" and "outlet" must be coincident with each other within the limits of error, *i.e.* $\pm 0.01\%$ N¹⁵, stated by BOKHOVEN *et al.* (Ref. 9), of N¹⁵-determination, which are basic to the z_i -values. Fluctuation of z_i -values over the three points markedly in excess of the above limits in these two runs suggests some gross error involved there, which might be responsible for the above absurdity.

Stoichiometric Number of the Rate-Determining Step

and the mean values of z_i given in Table 3. The sixth row gives the value of ε_2 calculated by (28.a) using the value of $\bar{\kappa}$ deduced from data in fourth and fifth columns by (27.a) neglecting ε_2 . We see from the comparison of fifth and sixth rows with reference to (27.a), that ε_2 is too small to affect any significant figures or practically negligible. The second last row reproduces the values of $\bar{\kappa}$ thus calculated.

The value of ε_1 given in the third last row is that calculated by (28.b) on the base of $\bar{\kappa}$ given by (27.b) neglecting ε_1 . This value of ε_1 is not negligible as compared with $z_{1,\ell}^N - 2z_i(1 - z_i)$, given in the row right above, from which ε_1 is to be subtracted according to (27.b). The $\bar{\kappa}$ was now calculated again for the first approximation substituting the above value of ε_1 into the latter equation. The $\bar{\kappa}$ -value of the second approximation was calculated by (27.b) on the base of ε_1 -value computed by (28.b) from the $\bar{\kappa}$ -value of the first approximation. The $\bar{\kappa}$ of the second approximation, being found coincident with that of the first one in significant figures, was taken its final value as given in the last row of Table 4.

We see from the Table that $\bar{\kappa}$ -values derived either from the variation of z_2^N or from that of z_1^N agree with each other for each run and are unanimously greater than unity. This excludes on the one hand any possibility of (2.I) being the rate-determining step in accordance with (12.a) and on the other hand conforms approximately with the condition (12.b) for one of \mathcal{X} 's governing the rate. Step (2.II) is also excluded from being the rate-determining step, inasmuch as the rate of hydrogen exchange between ammonia and hydrogen in the presence of the same catalyst is immeasurably large at the present condition in question, as extrapolated from observations at lower temperatures¹³⁾.

The latter step is not however very distinctly characterized as a rate-determining step, $\bar{\kappa}$ being not large enough. The similar conclusion has been arrived at⁸⁾ by the analysis of the hysteresis of the catalyzed decomposition of ammonia mentioned in the introduction, that N(a) formed by the reversal of (2.III) in this case is not in complete equilibrium with N_2 because of the above situation but its activity increases above that corresponding to the equilibrium with increase of the decomposition rate along with increase of the ammonia partial pressure, until the activity attains its amount at the equilibrium of γ' -phase (Fe_4N) and α -phase; the catalyst turns then into γ' -phase, at somewhat higher ammonia partial pressure than corresponding to the latter phase equilibrium, thus giving rise to the stable hysteresis^{8)*}.

Summary

1. The report of BOKHOVEN *et al.*⁹⁾, that the stoichiometric number $\nu(r)$ of the rate-determining step of the catalyzed ammonia synthesis $N_2 + 3H_2 = 2NH_3$ in the presence of commercial synthetic catalyst was 1, which contradicts our

*) The sequence of steps has been slightly modified (Ref. 8) from that of (2), which matters however scarcely the present argument.

previous conclusion¹⁾²⁾⁸⁾ that $\nu(r)=2$, was investigated with special reference to the procedure of deducing $\nu(r)$ from their experimental results.

2. It was shown that $\nu(r)$ decreases, according to their procedure of its evaluation, extraordinarily sensitively with decrease of the value of the ammonia mol fraction x_e^A in gas mixture at equilibrium of the above synthetic reaction and the ammonia mol fraction observed for a prolonged contact time, taken by them to be x_e^A , was definitely smaller than the true value, hence that the value 1 of $\nu(r)$ as reported by them is virtually a lower bound.

3. Their simultaneous observations on the mol fractions of N_2^{30} and N_2^{29} in nitrogen as well as of $N^{15}H_3$ in ammonia varying through contact with the catalyst were analyzed for the valid rate-determining step by a procedure not suffering from the ambiguity of x_e^A mentioned in 2. Inevitable conclusion of the analysis was that the rate-determining step was by no means the step $N_2 \rightarrow 2N(a)[(a): \text{adsorbed state}]$, contradicting their conclusion, but one of the subsequent steps, $N(a) + H(a) \rightarrow NH(a)$, $NH(a) + H(a) \rightarrow NH_2(a)$ and $NH_2(a) + H(a) \rightarrow NH_3$, for which $\nu(r)=2$, in accordance with our previous conclusion¹⁾²⁾.

Acknowledgements

The present authors express their sincere thanks to Dr. T. TOYA, Dr. A. MATSUDA, Mr. G. TODA and Mr. T. KODERA for their kind interests and valuable discussions to the present work.

Appendix I

Errors of $\nu(r)$ Caused by the Approximations of BOKHOVEN *et al*⁹⁾.

BOKHOVEN *et al*.⁹⁾ deduced $\nu(r)$, as mentioned in the introduction, from data of synthesis rate observed at constant pressure and of exchange rate at incomplete equilibrium, identifying them with those observed respectively at constant volume and at complete equilibrium. Errors of $\nu(r)$ caused by these approximations are numerically estimated as below on the basis of the exact expression of $\nu(r)$.

The exact numerical determination of $\nu(r)$ allowed for the incomplete equilibrium requires, however, the detailed knowledge of the forward and the backward unidirectional rates in the neighbourhood of the equilibrium of (1). This being not available, the exact expression is derived in Appendix II, under a plausible assumption that the forward rate \bar{V} decreases and backward one \bar{V} increases, as the equilibrium of the synthesis is approached, finally to coincide with each other at $\bar{V}_e = \bar{V}_e$ where e signifies the quantities at equilibrium or that $\bar{V}_e = \bar{V}_e$ lies between any momentary values of \bar{V} and \bar{V} , as

Stoichiometric Number of the Rate-Determining Step

$$\nu(r) = \frac{\left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} - \frac{4}{m_e}\right) \left\{ \ln \frac{z_0^\Lambda - z_t}{z_t^\Lambda - z_t} - \bar{\theta}(\bar{a} + \bar{n})t \right\}}{\left(\frac{2}{a_e} + \frac{1}{n_e}\right) \left(\ln \frac{x_e^\Lambda - x_0^\Lambda}{x_e^\Lambda - x_t^\Lambda} + \bar{m}t \right) + \left(\frac{2\bar{a}}{a_e} - \frac{\bar{n}}{n_e}\right)t}, \quad 0 \leq \bar{\theta} \leq 1 \quad (\text{i. P})$$

for the constant pressure and

$$\nu(r) = \frac{\left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e}\right) \left\{ \ln \frac{z_0^\Lambda - z_t}{z_t^\Lambda - z_t} - \bar{\theta}(\bar{a} + \bar{n})t \right\}}{\left(\frac{2}{a_e} + \frac{1}{n_e}\right) \left(\ln \frac{x_e^\Lambda - x_0^\Lambda}{x_e^\Lambda - x_t^\Lambda} + \bar{m}t \right) + \left(\frac{2\bar{a}}{a_e} - \frac{\bar{n}}{n_e}\right)t}, \quad 0 \leq \bar{\theta} \leq 1 \quad (\text{i. V})$$

for the constant volume respectively of the definite portion of the gas mixture referred to in §4, where

$$m = a + n + h, \quad (\text{ii})$$

$$\bar{m} = \frac{1}{t} \ln \frac{m_e + 2\Delta_0}{m_e + 2\Delta_t}, \quad \bar{a} = \frac{1}{t} \ln \frac{a_e - 2\Delta_t}{a_e - 2\Delta_0}, \quad n = \frac{1}{t} \ln \frac{n_e + \Delta_0}{n_e + \Delta_t},$$

(iii. m), (iii. a), (iii. n)

$$a = a_e - 2\Delta, \quad n = n_e + \Delta, \quad h = h_e + 3\Delta, \quad (\text{iv. a}), (\text{iv. n}), (\text{iv. h})$$

a , n and h are numbers of mols of ammonia, nitrogen and hydrogen in that portion and suffix 0 or t signifies the quantities at the beginning or at the end of the contact time t .

Eq.(i) shows that $\nu(r)$ lies between two values respectively for $\bar{\theta}=0$ and $\bar{\theta}=1^*$) either at constant pressure or volume, corresponding to the above postulate that $\vec{V}_e = \vec{V}_e$ lies between \vec{V} and \vec{V} . The Δ gives the "distance" to the equilibrium in accordance with (iv) and (1) in terms of the amount of each component contained in the definite portion of the gas mixture. At equilibrium of (1), where $\Delta_0 = \Delta_t = 0$, \bar{m} , \bar{a} and \bar{n} vanish according to (iii), hence (i.P) reduces to the form

$$\nu(r) = \frac{\left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} - \frac{4}{m_e}\right) \ln \frac{z_0^\Lambda - z_t}{z_t^\Lambda - z_t}}{\left(\frac{2}{a_e} + \frac{1}{n_e}\right) \ln \frac{x_e^\Lambda - x_0^\Lambda}{x_e^\Lambda - x_t^\Lambda}}, \quad (\text{v})$$

while (i.V) exactly to (3), inasmuch as a_e etc. are respectively proportional to the appropriate partial pressures.

The term $4/m_e$, by which the expression of $\nu(r)$ at constant pressure differs from that at constant volume, makes however numerically but a trifling difference of ca. 2% of $\nu(r)$, m_e being ca. 50 times as large as a_e at the

*) Cf. Appendix II.

condition of BOKHOVEN *et al.*'s experiment⁹⁾.

The value of $\nu(r)$ are computed as below by (3) and by (i. V) for $\bar{\theta}=0$ as well as $\bar{\theta}=1$, with the run quoted in the first column of Table 1.

$\nu(r)$ computed by (3) or (i. v).

Computed by	(3)	(i. v) for $\bar{\theta}=0$	(i. v) for $\bar{\theta}=1$
$\nu(r)$	1.15	1.07	0.91

The $\nu(r)$ for constant pressure is obtained in the respective case by decreasing the above values each by 2% according to the above. The example shows that the neglect of incomplete attainment to equilibrium makes $\nu(r)$ too large by less than 27%, apart from the associated deficiency of x_e^A , which makes $\nu(r)$ exceedingly too small as shown in §1.

Appendix II

Exact Equation of $\nu(r)$

Formulation of $\nu(r)$

The $\nu(r)$ is formulated below allowing for the incomplete equilibrium.

We start from the general equation, which holds in the case of overall reaction of a single route^{*)} with a rate-determining step r , *i.e.*

$$\nu(r) = - \frac{\Delta F}{RT \ln(\bar{V}/\bar{V})}, \quad (\text{vi})$$

where ΔF is the free energy increase appropriate to the chemical equation of the overall reaction, to which $\nu(r)$ is referred. ΔF is *e.g.* for (1)

$$\Delta F = 2\mu^A - \mu^N - 3\mu^H, \quad (\text{vii})$$

where μ^A , μ^N and μ^H are chemical potentials respectively of ammonia, nitrogen and hydrogen in gas.

Eq.(vi) is derived for the overall reaction of a single route with a rate-determining step from the general equation for the forward and backward rates, \bar{v} and \bar{v} , of thermal step⁴⁾¹⁴⁾

$$\bar{v} = \frac{kT}{h} p^*/p^I, \quad \bar{v} = \frac{kT}{h} p^*/p^F,$$

where p^I or p^F is the BOLTZMANN factor of the chemical potential μ^I or μ^F of the initial or the final complex of the step, *i.e.*

*) Cf. §3.

Stoichiometric Number of the Rate-Determining Step

$$p^I = \exp(-\mu^I/kT)$$

or

$$p^F = \exp(-\mu^F/kT),$$

p^* that of the critical complex and k or h the BOLTZMANN or PLANCK constant. We have from the above four equations for any constituent step s of the overall reaction

$$\bar{v}(s)/\bar{v}(s) = \exp(-\Delta F_s/RT), \quad (\text{viii})$$

where ΔF_s is the free energy increase $\mu^F - \mu^I$ associated with the step.

The free energy increase ΔF of the overall reaction is now given in accordance with the definition of $\nu(s)$ as

$$\Delta F = \sum_{s=1}^S \nu(s) \Delta F_s,$$

which reduces to the form

$$\Delta F = \nu(r) \Delta F_r, \quad (\text{ix})$$

since according to (6) and (viii), approximately

$$\Delta F_s = 0, \quad s \neq r. \quad (\text{x})$$

Writing (viii) particularly for r as

$$\bar{v}(r)/\bar{v}(r) = \exp(-\Delta F_r/RT),$$

we have (vi) by eliminating $\bar{v}(r)$, $\bar{v}(r)$ and ΔF_r from (7.a), (7.b), (ix) and the above equation.

The $\nu(r)$ may be determined by (vi) directly from data of ΔF , \vec{V} and \vec{V} as did by HORIUTI and MATSUDA¹⁵⁾ from the observations of LOSEV¹⁶⁾ on the electrode reaction of zinc amalgam. Initially, however, $\nu(r)$ was formulated for its experimental determination with special reference to the equilibrium of the overall reaction¹⁾²⁾. The latter procedure will be developed below to derive the exact expression (i) valid around the equilibrium.

At the equilibrium, where $\Delta F = 0$ and $\vec{V} = \vec{V}$ (vi) reduces to the form 0/0. The $\nu(r)$ is evaluated there as its limiting value of the ratio of the differential coefficient with respect to ΔF of the numerator to that of the denominator, as

$$\begin{aligned} \nu(r) &= \lim_{\Delta F \rightarrow 0} -\Delta F/RT (\ln \vec{V}/\vec{V}) = \frac{1}{RT} \left\{ -\frac{1}{\vec{V}} \frac{\partial \vec{V}}{\partial \Delta F} + \frac{1}{\vec{V}} \frac{\partial \vec{V}}{\partial \Delta F} \right\}_e^{-1} \\ &= -\vec{V}_e/RT (\partial V/\partial \Delta F)_e \end{aligned} \quad (\text{xi})$$

with reference to (8), noting that $\vec{V}_e = \vec{V}_e$. The $(\partial V/\partial \Delta F)_e$ and \vec{V}_e in (xi) are now developed with special reference to (1) as follows.

$$\frac{(\partial V/\partial \Delta F)_e}{\vec{V}_e}$$

The $(\partial V/\partial \Delta F)_{\Delta_e=0}$ is rewritten as

$$(\partial V/\partial \Delta F)_e = (\partial V/\partial \Delta)_e / (\partial \Delta F/\partial \Delta)_e. \quad (\text{xii})$$

We have from (1) and (iv)

$$V = -\partial \Delta / \partial t \quad (\text{xiii})$$

or

$$V/\Delta = -\partial \ln \Delta / \partial t .$$

The limiting value of the left-hand side of the above equation at the equilibrium is given similarly as in the case of (xi) as $(\partial V/\partial \Delta)_e$, hence

$$(\partial V/\partial \Delta)_e = -(\partial \ln \Delta / \partial t)_e .$$

According to the linear relation of $\ln \Delta$ to t observed around equilibrium in the previous works^{1,2)}, $\partial \ln \Delta / \partial t$ is constant there, so that we have from the above equation,

$$(\partial V/\partial \Delta)_e = -\partial \ln \Delta / \partial t$$

or by integration

$$k_s \equiv (\partial V/\partial \Delta)_e = \frac{1}{t} \ln \frac{\Delta_0}{\Delta_t} , \quad (\text{xiv. a})$$

hence

$$\Delta = \Delta_0 \exp(-k_s t) . \quad (\text{xiv. b})$$

The k_s is expressed according to (xiv.a) in terms of x^Λ , x_0^Λ and x_e^Λ as follows. We have from (ii) and (iv)

$$m = m_e + 2\Delta ,$$

$$x^\Lambda = \frac{a}{m} = \frac{a_e - 2\Delta}{m_e + 2\Delta} , \quad x^N = \frac{n}{m} = \frac{n_e + \Delta}{m_e + 2\Delta} , \quad x^H = \frac{h}{m} = \frac{h_e + 3\Delta}{m_e + 2\Delta} .$$

$$(\text{xv. A}), (\text{xv. N}), (\text{xv. H})$$

$$x_e^\Lambda = a_e / m_e , \quad (\text{xv. e})$$

hence

$$\frac{x_e^\Lambda - x_0^\Lambda}{x_e^\Lambda - x^\Lambda} = \frac{m_e + 2\Delta}{m_e + 2\Delta_0} \frac{\Delta_0}{\Delta} . \quad (\text{xv. f})$$

The $(\partial V/\partial \Delta)_e$ is now given by (xiv.a) and (xv.f) as

$$\left(\frac{\partial V}{\partial \Delta} \right)_e \equiv k_s = \frac{1}{t} \ln \frac{\Delta_0}{\Delta_t} = \frac{1}{t} \ln \frac{x_e^\Lambda - x_0^\Lambda}{x_e^\Lambda - x_t^\Lambda} + \bar{m} \quad (\text{xvi})$$

with reference to (iii.m).

The $(\partial \Delta F/\partial \Delta)_e$ in (xii) is given in terms of observable quantities by (vii) and the expressions of chemical potentials,

Stoichiometric Number of the Rate-Determining Step

$$\mu^A = \mu_i^A + RT \ln P^A, \quad \mu^N = \mu_i^N + RT \ln P^N, \quad \mu^H = \mu_i^H + RT \ln P^H,$$

as

$$\left(\frac{\partial \Delta F}{\partial \Delta}\right)_e = RT \left(-\frac{2}{P^A} \frac{\partial P^A}{\partial \Delta} - \frac{1}{P^N} \frac{\partial P^N}{\partial \Delta} - \frac{3}{P^H} \frac{\partial P^H}{\partial \Delta} \right), \quad (\text{xvii})$$

where P^A etc. are partial pressures of ammonia etc. and μ_i^A etc. the values of μ^A etc. at $P^A=1$ etc. respectively. The $(\partial \Delta F / \partial \Delta)_e$ is evaluated^{10,11} separately for the case of constant pressure or volume of the definite portion of the gas mixture*).

The partial pressures are given, in terms of total pressure P_T , as

$$P^A = P_T x^A, \quad P^N = P_T x^N, \quad P^H = P_T x^H.$$

In the case of constant total pressure we have with reference to (xv)

$$\left(\frac{1}{P^A} \frac{\partial P^A}{\partial \Delta}\right)_e = -\frac{2}{a_e} - \frac{2}{m_e}, \quad \left(\frac{1}{P^N} \frac{\partial P^N}{\partial \Delta}\right)_e = \frac{1}{n_e} - \frac{2}{m_e}, \quad \left(\frac{1}{P^H} \frac{\partial P^H}{\partial \Delta}\right)_e = \frac{3}{h_e} - \frac{2}{m_e},$$

since $\Delta=0$ at equilibrium. Substituting $\left(\frac{1}{P^A} \frac{\partial P^A}{\partial \Delta}\right)_e$ etc. from the above equations into (xvii), we have

$$\left(\frac{\partial \Delta F}{\partial \Delta}\right)_e = -RT \left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} - \frac{4}{m_e} \right). \quad (\text{xviii. P})$$

In the case of constant volume, P^A etc. are respectively proportional to a etc., so that $\left(\frac{1}{P^A} \frac{\partial P^A}{\partial \Delta}\right)_e$ etc. equal $\left(\frac{1}{a} \frac{\partial a}{\partial \Delta}\right)_e$ etc. respectively. The $(\partial \Delta F / \partial \Delta)_e$ is now given by (xvii) and (iv) as

$$\left(\frac{\partial \Delta F}{\partial \Delta}\right)_e = -RT \left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} \right), \quad (\text{xviii. V})$$

which differs from that for constant pressure by the term $4/m_e$ in the parentheses.

The differential coefficient $(\partial V / \partial \Delta F)_e$ is now given by substituting $(\partial V / \partial \Delta)_e$ from (xvi) and $(\partial \Delta F / \partial \Delta)_e$ either from (xviii.P) or (xviii.V) into (xii), according as the definite portion of gas mixture is kept at constant pressure or volume respectively, as

$$1 / \left(\frac{\partial V}{\partial \Delta F} \right)_e = -\frac{RT}{k_s} \left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} - \frac{4}{m_e} \right) \text{ (constant pressure),} \quad (\text{xix. P})$$

$$1 / \left(\frac{\partial V}{\partial \Delta F} \right)_e = -\frac{RT}{k_s} \left(\frac{4}{a_e} + \frac{1}{n_e} + \frac{9}{h_e} \right) \text{ (constant volume).} \quad (\text{xix. V})$$

* Cf. §4.

\vec{V}_e

We start from the equation

$$d(az^A)/dt = 2\vec{V}z^N - 2\vec{V}z^A,$$

which is exact, even besides at equilibrium, on the basis of the postulates (a), (b) and (c) in §3; the left-hand side is the total rate $d(az^A)/dt$ of increase of N^{15} in ammonia and the right-hand side is the excess of the forward unidirectional rate $2\vec{V}z^N$ of N^{15} transferred from nitrogen to ammonia over the backward one $2\vec{V}z^A$. The above equation is written in the form

$$z^A \frac{da}{dt} + a \frac{dz^A}{dt} = 2\vec{V}z^N - 2\vec{V}z^A.$$

The da/dt in this equation is expressed according to (b), §3, as

$$\frac{da}{dt} = 2\vec{V} - 2\vec{V}. \quad (\text{xx})$$

We have from the last two equations*)

$$a \frac{dz^A}{dt} = 2\vec{V}(z^N - z^A) \quad (\text{xxi})$$

*) Eq. (xxi) is derived alternatively from (18) as below. Substituting κ from (16.c) and $\vec{V}_1 + \vec{V}_2$ from (14.a) into (18), we have

$$n \frac{dz^N}{dt} = \frac{\vec{V}_1 \vec{V}_2}{\vec{V}_1 + \vec{V}_2} (z^A - z^N),$$

where $\vec{V}_2 \cdot \vec{V}_1 / (\vec{V}_1 + \vec{V}_2)$ is half the unidirectional rate of formation of $N(a)$ from NH_3 , *i.e.* \vec{V}_2 multiplied by the ratio $\vec{V}_1 / (\vec{V}_1 + \vec{V}_2)$ of the rate $2\vec{V}_1$ of $N(a)$ being turned into N_2 over the total rate $2(\vec{V}_1 + \vec{V}_2)$ of conversion of $N(a)$, or the half the backward unidirectional rate of NH_3 to convert into N_2 , or the backward unidirectional rate \vec{V} of (1), *i.e.*

$$\vec{V} = \vec{V}_2 \vec{V}_1 / (\vec{V}_1 + \vec{V}_2),$$

hence

$$n \frac{dz^N}{dt} = \vec{V}(z^A - z^N).$$

The differentiation of (19) with respect to time gives

$$2 \frac{dn}{dt} z^N + 2n \frac{dz^N}{dt} + \frac{da}{dt} z^A + a \frac{dz^A}{dt} = 0,$$

where dn/dt and da/dt are expressed as

$$\frac{dn}{dt} = \vec{V} - \vec{V}, \quad \frac{da}{dt} = 2\vec{V} - 2\vec{V}.$$

Eq. (xxi) is obtained by eliminating dz^N/dt , dn/dt and da/dt from the above four equations.

or eliminating z^N from (xxi) and (19)

$$\frac{dz^A}{dt} = \frac{\vec{V}}{an} \{ \bar{n}^{1s} - (2n+a)z^A \}. \quad (\text{xxii})$$

Eq.(xxii) is integrated, observing that n^{1s} as well as $2n+a$ is constant in course of reaction and referring to (20.c), as

$$\frac{1}{t} \ln \frac{z_0^A - z_i}{z_i^A - z_i} = \frac{2n+a}{t} \int_0^t \frac{\vec{V}}{an} dt. \quad (\text{xxiii})$$

In the special case when the equilibrium of (1) is established, we have $\vec{V} = \vec{V}_e$, $a = a_e$ and $n = n_e$, so that (xxiii) reduces to the form

$$\frac{1}{t} \ln \frac{z_0^A - z_i}{z_i^A - z_i} = \left(\frac{2}{a_e} + \frac{1}{n_e} \right) \vec{V}_e. \quad (\text{xxiv})$$

The general equation (xxiii) is now developed in accordance with the assumption referred to in Appendix I that \vec{V}_e lies between \vec{V} and \bar{V} , which is expressed as

$$\vec{V} = \vec{V}_e + \theta(\vec{V} - \bar{V}), \quad 0 \leq \theta \leq 1 \quad (\text{xxv})$$

or according to (8) as

$$\vec{V} = \vec{V}_e + \theta V.$$

Expressing V by (xiii) and (xiv.b) as $V = k_s \Delta$, we have

$$\vec{V} = \vec{V}_e + \theta k_s \Delta. \quad (\text{xxvi})$$

Substituting \vec{V} , a and n into (xxiii) respectively from (xxvi), (iv.a) and (iv.n), and replacing dt there with $-d\Delta/k_s \Delta$ according to (xiv.b), we have

$$\frac{1}{t} \ln \frac{z_0^A - z_i}{z_i^A - z_i} = \frac{(2n+a)\vec{V}_e}{k_s t} \int_{j_0}^{j_t} \frac{d\Delta}{\Delta(a_e - 2\Delta)(n_e + \Delta)} + \frac{2n+a}{t} \int_{j_0}^{j_t} \frac{\theta d\Delta}{(a_e - 2\Delta)(n_e + \Delta)}$$

or carrying through the integration with reference to (iii)

$$\frac{1}{t} \ln \frac{z_0^A - z_i}{z_i^A - z_i} = \vec{V}_e \left(\frac{1}{n_e} + \frac{2}{a_e} - \frac{\bar{n}}{n_e k_s} + \frac{2\bar{a}}{a_e k_s} \right) + \bar{\theta}(\bar{a} + \bar{n}), \quad (\text{xxvii})$$

where

$$\bar{\theta} = \int_{j_0}^{j_t} \frac{\theta d\Delta}{(a_e - 2\Delta)(n_e + \Delta)} \bigg/ \int_{j_0}^{j_t} \frac{d\Delta}{(a_e - 2\Delta)(n_e + \Delta)}.$$

It follows from the above definition of $\bar{\theta}$ and (xxv) that

$$0 \leq \bar{\theta} \leq 1,$$

inasmuch as $1/(a_e - 2\Delta)(n_e + \Delta)$ or $1/an$ by (iv) is constantly positive throughout

over the range of integration.

The exact expression (i) of $\nu(r)$ is obtained by substituting $(\partial V/\partial \Delta F)_c$ and \bar{V}_c into (xi) respectively from (xix) and (xxvii) and expressing k_c implied in (xxvii) by the last member of (xvi).

References

- 1) S. ENOMOTO and J. HORIUTI, This Journal **2**, 87 (1951-3); Proc. Japan Acad. **28**, 493 (1952).
- 2) S. ENOMOTO, J. HORIUTI and H. KOBAYASHI, this Journal **3**, 155 (1953-5).
- 3) J. HORIUTI and M. IKUSIMA, Proc. Imp. Acad. Tokio **15**, 39 (1939).
- 4) J. HORIUTI, "*The Theory of Reaction Rate*", Iwanami Book Co. Tokio (1940).
- 5) J. HORIUTI and T. NAKAMURA, Z. physik. Chem. (Neue Folge) **11**, 358 (1957).
J. HORIUTI, this Journal **5**, 1 (1957).
- 6) J. HORIUTI, "*Advances in Catalysis*", Academic Press, Inc. New York IX, 339 (1957);
Z. physik. Chem. (Neue Folge) **12**, 321 (1957). T. NAKAMURA and H. YAMAZAKI,
this Journal **5**, 98 (1957). T. NAKAMURA, this Journal **6**, 20 (1958).
- 7) J. HORIUTI and I. TOYOSHIMA, this Journal **5**, 120 (1957), **6**, 68 (1958).
- 8) I. TOYOSHIMA and J. HORIUTI, this Journal **6**, 146 (1958).
- 9) C. BOKHOVEN, M. J. GORGELS and P. MARS, Trans. Faraday Soc. **55**, 315 (1959).
- 10) J. HORIUTI and S. ENOMOTO, Proc. Japan Acad. **29**, 164 (1953).
- 11) J. HORIUTI, Proc. Japan Acad. **29**, 160 (1953).
- 12) F. HABER, Z. Elektrochem. **20**, 603 (1914).
- 13) S. ENOMOTO, "*Catalysis*" **8**, 47 (1952).
- 14) J. HORIUTI, Bull. Chem. Soc. Japan **13**, 210 (1938). K. HIROTA and J. HORIUTI, Sci.
Papers Inst. Phys. Chem. Research, Tokyo **34**, 1174 (1938).
- 15) J. HORIUTI and A. MATSUDA, this Journal **7**, 19 (1959).
- 16) V. V. LOSEV, Collected Works Inst. Phys. Chem. Acad. Sci. USSR **6**(2),20 (1957).