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<td>TANAKA, Kazunori</td>
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THE RATE-DETERMINING STEP OF AMMONIA
SYNTHESIS AND DECOMPOSITION

Part 1. Study of the Reaction over Singly-Promoted
Iron Catalyst at 305 and 340°C*

By
Kazunori Tanaka**
(Received October 10, 1965)

Abstract
Kinetic investigation has been made of ammonia synthesis and decomposition using N\textsuperscript{15} as
tracer over a singly-promoted iron catalyst at a total pressure of 550 mmHg and at 305 and 340°C.
It was found that during the catalyzed ammonia synthesis or decomposition, the chemisorbed
nitrogen is in partial equilibrium with the gaseous ammonia but not with the gaseous nitrogen.
It may therefore be concluded that nitrogen chemisorption and desorption are rate-determining
for catalyzed ammonia synthesis and decomposition respectively. In decomposition, the observed
values for \( \nu \) (the stoichiometric number of the rate-determining step) were close to unity with
reference to the overall reaction, \( 3H_2 + N_2 = 2NH_3 \), providing further evidence for nitrogen
desorption being rate-determining. In synthesis, however, the observed \( \nu \) values were appreciably
lower than unity and decreased to zero with increasing chemical affinity. It is preliminarily
noticed that this peculiar behavior of \( \nu \) can be explained as resulting from the observed adsorp-
tion of ammonia on the catalyst and on the walls of apparatus during the ammonia synthesis
or decomposition.

Introduction
A previous paper\(^1\) outlined a new method for determining the rate-deter-
mining step in catalyzed ammonia synthesis and decomposition

\[
3H_2 + N_2 = 2NH_3 \quad (1)
\]

using N\textsuperscript{15} on the assumption that the reaction proceeded through the sequence of steps

\[
\begin{align*}
N_2 & \rightleftharpoons 2N(a) \quad 1 \quad (2. I) \\
H_2 & \rightleftharpoons 2H(a) \quad 3 \quad (2. II)
\end{align*}
\]

\(^*\) Part of this paper was presented at "The 16th Annual Meeting of the Chemical Society
of Japan" held in Tokyo, Japan, April 2, 1963.

**\) Research Institute for Catalysis, Hokkaido University, Japan.
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\[
\begin{align*}
N(a) + H(a) &\rightleftharpoons NH(a) & 2 \\
NH(a) + H(a) &\rightleftharpoons NH_2(a) & 2 \\
NH_2(a) + H(a) &\rightleftharpoons NH_3 & 2
\end{align*}
\]

(2. III)

where (a) signifies the adsorbed state. The number of the right of each step is its stoichiometric number, i.e. the number of times an elementary step occurs in every completed overall reaction. The new method consists in determining the stoichiometric number \( \nu_r \) of the rate-determining step and simultaneously deciding whether \( N_2 \) or \( NH_3 \) is in partial equilibrium with \( N(a) \). A detailed description of this method is given in the present paper.

Ammonia synthesis and decomposition were studied by this method using 1.51 g of a singly-promoted iron catalyst at 305 and 340°C, and then by using 0.32 g of a different portion of the same catalyst at 360 and 390°C. The later investigations at higher temperatures have been previously reported. The observed \( \nu_r \) values were thus found close to unity in most cases and \( NH_3 \) rather than \( N_2 \) in partial equilibrium with \( N(a) \), indicating that step (2. I) is rate-determining. The earlier investigations at lower temperatures are described in this paper. In the course of the ammonia synthesis and decomposition it was found that an appreciable amount of ammonia was adsorbed on the catalyst and on the walls of the apparatus. This adsorption is also discussed in some detail in the present paper.

1. Theoretical

1.1. System Being Considered. A mixture of hydrogen, nitrogen and ammonia is circulated over an ammonia synthesis catalyst; either nitrogen or ammonia is labeled with \( N^{15} \); the pressure of the ammonia and the transfer of \( N^{15} \)-atoms from nitrogen to ammonia or vice versa are followed at a constant total pressure until the ammonia synthesis or decomposition attains equilibrium. With this system, a few equations are derived to evaluate \( \nu_r \) as is described in section 1.2.

In section 1.3, this system is specified in such a way (i) that throughout the reaction the pressures of the hydrogen and nitrogen are practically constant and much greater than that of the ammonia and (ii) at the start of the reaction the nitrogen is normal while the ammonia is labeled with \( N^{15} \) to an \( N^{15} \)-atomic fraction of close to unity. With the system thus specified, two functions are defined which decide whether gaseous nitrogen or ammonia is in partial equilibrium with \( N(a) \). It is expedient to add that with this specified system both \( \nu_r \) and partial equilibrium can simultaneously be determined in a single experiment.
The Rate-Determining Step of Ammonia Synthesis and Decomposition Part 1.

It has been tacitly assumed with these systems that throughout the reaction, none of the reaction mixture is withdrawn from the system. This is not the case in the experiments described in later sections of this paper. Actually, a representative sample of the mixture was occasionally withdrawn from the reaction system, although throughout the reaction the total pressure was kept constant by reducing the volume of the system when the sample was taken. It is demonstrated in section 1.4 that successive samplings do not affect the determinations of the $\nu_r$ and partial equilibrium.

1.2. Stoichiometric Number of Rate-Determining Step. In the presence of a rate-determining step we have the general relation:\(^{3}\)

$$\nu_r = \frac{-\Delta F}{RT \ln (V_+/V_-)} , \tag{3}$$

where $-\Delta F$ is the chemical affinity of the overall reaction (1), $R$ is the gas constant, $T$ is the reaction temperature, and $V_+$ and $V_-$ are the unidirectional forward and backward rates respectively. Eq. (3) may be written in other forms which consist solely of directly observable quantities and is applicable to the present experiments.

The chemical affinity may be given in terms of the equilibrium constant $K_s$ for the reaction (1) and the pressures $P_H$, $P_N$ and $P_A$ respectively of hydrogen, nitrogen and ammonia as

$$-\Delta F = RT \ln \left( \frac{P_H^a P_N^b}{P_A^a} K_s \right) . \tag{4}$$

The overall reaction rate $V$ may be written as

$$V = V_+ - V_- = \frac{1}{2} \frac{da}{dt} = -\frac{dn}{dt} , \tag{5. a}$$

where $a$ is the total number of moles of ammonia, $N^{14}H_3$ and $N^{15}H_3$, $n$ is that of nitrogen, $N^{14}N^{14}$, $N^{14}N^{15}$ and $N^{15}N^{15}$, and $t$ is time. The rate of $N^{15}$-transfer from nitrogen to ammonia or vice versa may be given by

$$\frac{d(Z^a a)}{dt} = 2(Z^a V_+ - Z^a V_-) \tag{6. a}$$

or

$$\frac{d(Z^n n)}{dt} = Z^a V_+ - Z^n V_- , \tag{6. b}$$
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where $Z^A$ and $Z^N$ are the $N^{15}$-atomic fractions of ammonia $N^{15}H/(N^{15}H_2+N^{15}H_3)$ and nitrogen $(N^{15}N^{14}+2N^{15}N^{14})/(N^{15}N^{14}+N^{15}N^{15}+N^{15}N^{15})$ respectively. Combining Eqs. (5.a) and (6.a) we have

$$\frac{V_+}{V_-} = \frac{a \frac{dZ^A}{dt} / 2(Z^N - Z^A)}{\left\{ a \frac{dZ^A}{dt} / 2(Z^N - Z^A) \right\} - \frac{1}{2} \frac{da}{dt}}$$

or

$$\frac{1}{1-(Z^N - Z^A) \frac{d\ln P_A}{dZ^A}}$$

insofar as $a$ is proportional to $P_A$. Substituting $-\Delta F$ and $V_+/V_-$ respectively from Eqs. (4) and (7.b) into (3) we obtain

$$\frac{RT \ln \left( \frac{P_A P_N}{P_A} K_s \right)}{RT \ln \left\{ 1 - (Z^N - Z^A) \frac{d\ln P_A}{dZ^A} \right\} \frac{1}{2} \frac{da}{dt}}$$

which enables us to evaluate $\nu_\nu$ at any stage of ammonia synthesis and decomposition. On the other hand, solving Eqs. (5.b) and (6.b) for $V_+$ and $V_-$ and replacing $dn/dt$ in the expression of $V_+$ by $-\frac{1}{2} \cdot da/dt$ with reference to Eqs. (5)

$$\frac{V_+}{V_-} = \frac{n \frac{dZ^N}{dt} / (Z^N - Z^A) + \frac{1}{2} \frac{da}{dt}}{n \frac{dZ^N}{dt} / (Z^N - Z^A)}$$

or

$$1 + \frac{P_A}{2P_N} (Z^N - Z^A) \frac{d\ln P_A}{dZ^N}$$

Thus we obtain another equation for evaluating $\nu_\nu$, i.e.

$$\nu_\nu = \frac{RT \ln \left( \frac{P_A P_N}{P_A} K_s \right)}{RT \ln \left\{ 1 + \frac{P_A}{2P_N} (Z^N - Z^A) \frac{d\ln P_A}{dZ^N} \right\} \frac{1}{2} \frac{da}{dt}}$$

At a time during the course of ammonia synthesis or decomposition we have

$$Z^A a + 2Z^N n = Z_i (a + 2n)$$

or in terms of pressures

$$Z^A P_A + 2Z^N P_N = Z_i (P_A + 2P_N)$$

where $Z_i$ is the value of $Z^A$ or $Z^N$ in exchange equilibrium of $N^{15}$-atoms.
between nitrogen and ammonia. Elimination of $Z^N$ from Eq. (8) by use of Eq. (11.b) yields

$$
\nu_r = \frac{RT \ln \left( \frac{P_i^N P_S}{P_A^N K_N} \right)}{RT \ln \left[ \frac{1}{1 + \left( \frac{P_A}{2P_N} \right) (Z_{\text{n}} - Z_A) \frac{d \ln P_A}{dZ_A}} \right]}. \tag{12}
$$

This equation is useful in evaluating $\nu_r$ when $Z^N$ is unknown.

1.3. Partial Equilibrium. Provided that step (2. II) is fast enough, as is generally accepted, step (2. I) or one of steps (2. III) must be rate-determining depending upon whether the set of steps (2. III) or step (2. I) is in partial equilibrium and hence upon whether the $N^{15}$-atomic fraction $Z^{N(a)}$ of adsorbed nitrogen $N(a)$ is equal to $Z^A$ or to $Z^N$. Two functions $\phi$ and $\psi$ are introduced to decide which is the case in the system specified in section 1.1.

The $\phi$ is defined as

$$
\phi \equiv \frac{(Z_i^N)^2}{Z_i^N Z_i^N} / K_N, \tag{13}
$$

where $Z_i^N$, $Z_i^A$ and $Z_i^N$ are the mole fractions of $N^{14}N^{14}$, $N^{14}N^{15}$ and $N^{15}N^{15}$ in gaseous nitrogen respectively, and $K_N$ is the equilibrium constant for nitrogen isotopes equilibration, $N^{14}N^{14} + N^{15}N^{15} = 2N^{14}N^{15}$. At the beginning of the reaction, nitrogen is normal so that the value of $\phi$ is unity independent of which is rate-determining. If step (2. I) is in partial equilibrium, $\phi$ continues at unity throughout the reaction since in that case the numerator $(Z_i^N)^2/Z_i^N Z_i^N$ is always equal to $K_N$. If the set of steps (2. III) is alternatively in partial equilibrium, $\phi$ decreases toward zero from its initial value of unity as the reaction progresses, although it eventually rises to unity again through a minimum along with the approach to the isotopic equilibrium. This decrease in the value of $\phi$ is caused by more rapid formation of $N^{15}N^{15}$ than $N^{14}N^{15}$ in an early stage of the reaction where $Z^{N(a)}$ is close to unity, and by the amount of $N^{14}N^{14}$ far exceeding the amounts of $N^{15}N^{15}$ and $N^{14}N^{15}$ throughout the reaction.

The rates of formation of $N^{14}N^{15}$ and $N^{15}N^{15}$, i.e. $d(Z_i^N)/dt$ and $d(Z_i^N)/dt$, are given with reference to step (2. I) as

$$
\frac{dZ_i^N}{dt} + n \frac{dZ_i^N}{dt} = 2Z_{\text{n}}(1 - Z_{\text{n}}) \nu_{-1} - Z_i^N \nu_{+1} \tag{14. a}
$$

and

$$
\frac{dZ_i^N}{dt} + n \frac{dZ_i^N}{dt} = (Z_{\text{n}})^2 \nu_{-1} - Z_i^N \nu_{+1} \tag{14. b}
$$

respectively, where $\nu_{-1}$ is the unidirectional forward rate of step (2. I) and $\nu_{+1}$.
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is the backward one. The first terms $Z_1^n dn/dt$ and $Z_2^n dn/dt$ are negligible in comparison with $ndZ_1^n/dt$ and $ndZ_2^n/dt$ respectively because $n$ is practically constant as specified in section 1.1. If the set of steps (2.III) is in partial equilibrium in an early stage of ammonia decomposition, $Z^A$ and hence $Z_1^{N(a)}$ are near unity and much greater than $Z^N$ so that the rates $Z_1^{N}v_{-1}$ and $Z_2^{N}v_{-1}$ are negligible in comparison with the respective reverse rates. Then, combining Eqs. (14.a) and (14.b), and equating $Z_1^{N(a)}$ to $Z^A$ yields

$$\frac{dZ_1^n}{dZ_1^n} = \frac{Z^A}{2(1-Z^A)}. \quad (15)$$

The function $\phi$ defined as

$$\phi = \frac{dZ_1^n}{dZ_2^n} = \frac{Z^A}{2(1-Z^A)} \quad (16)$$

is consequently equal to unity when the set of steps (2.III) is in partial equilibrium. The value of $\phi$ is, on the other hand, near zero when step (2.I) is in partial equilibrium because then the rate of formation of $N^{15}N^{15}$ is much less than the rate of formation of $N^{18}N^{18}$ since the value of $Z_1^{N(a)}$ is close to zero.

**Table 1.** Theoretical values for $\nu$, $\phi$ and $\phi$ thus theoretically derived for the alternative rate-determining step.

<table>
<thead>
<tr>
<th>Rate-determining step</th>
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<th>one of (2.III)</th>
<th>Stage of reaction where applicable</th>
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<td>Values for $\nu$</td>
<td>1</td>
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<td>valid throughout the reaction</td>
</tr>
<tr>
<td>Values for $\phi$</td>
<td>$\approx 0$</td>
<td>1</td>
<td>valid except in initial and final stages</td>
</tr>
<tr>
<td>Values for $\phi$</td>
<td>1</td>
<td>$\approx 0$</td>
<td>valid only in early stage of decomposition</td>
</tr>
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</table>

Table 1 summarizes values for $\nu$, $\phi$ and $\phi$ thus theoretically derived for the alternative rate-determining steps.

**1.4. No Effect of Sampling.** In previous section 1.2, three Eqs. (8), (10) and (12) have been derived for evaluating $\nu$ on the tacit assumption that none of the reaction mixture is withdrawn at any time during the reaction. The determination of partial equilibrium using $\phi$ is also based on this assumption. It is now proven that the proposed determinations of $\nu$ and partial equilibrium are valid even in cases where a representative portion of the reaction mixture is occasionally withdrawn as long as the volume of the reaction system is reduced at the time of the sampling so as to keep the total pressure constant. Differentiating both the numerator and denominator of $d\ln P_\lambda/dZ^A$ with respect to time,

$$\frac{d\ln P_\lambda}{dZ^A} = \frac{dP_\lambda/dt}{P_\lambda dZ^A/dt}. \quad (17)$$
The Rate-Determining Step of Ammonia Synthesis and Decomposition Part 1.

Eq. (5. a), on the other hand, may be rewritten in terms of pressure as

$$V = \frac{V_r}{2RT} \frac{dP_A}{dt}, \quad \text{(18)}$$

where $V_r$ is the volume of the reaction system. Solving Eqs. (5. a) and (6. a) for $V_r$ and applying Boyle's law to ammonia

$$V_r = \frac{P_A V_r}{2(Z^N - Z^A)RT} \frac{dZ^A}{dt}. \quad \text{(19)}$$

It is apparent from Eqs. (18) and (19) that both $dP_A/dt$ and $dZ^A/dt$ are inversely proportional to $V_r$. Successive samplings, therefore, vary the numerator and denominator of Eq. (17) by the same factor, exerting no influence upon $d\ln P_A/dZ^A$. It is also apparent that in Eq. (8) the variables other than $d\ln P_A/dZ^A$ are also unaffected by the successive samplings. The values for $\nu_r$ actually obtained using Eq. (8) are therefore equal to those which would result if no samples were taken. It may also be readily demonstrated that this is also true for Eqs. (10) and (12).

Successive samplings do not affect the values for $\phi$ and $\phi$ either. In the case of $\phi$, this is evident from Eq. (13) without demonstration. In the case of $\phi$, this can be proven by rewriting the term $dZ^A/dZ^N$ of Eq. (16) as $(dZ^A/dt)/(dZ^N/dt)$ and applying an argument similar to that made for $\nu_r$.

Fig. 1. Schematic diagram of the circulating system.

The broken lines enclose the circulating system, $S_c$. The circulating system, $S_c$, plus the reaction vessel, $R$, comprise the reaction system, $S_r$.
2. Experimental

2.1. Apparatus

Fig. 1 is a schematic diagram of the circulating system used to measure v_r, φ, and ϕ. The system consisted of the circulating pump P, vertical cylinder V, mercury manometer M, flow meter F, reaction vessel R, trap T, and U-tube U. Gas could be circulated through these, or through stopcocks C_2 and C_3 by-passing R and T. The circulating pump has four ground-glass valves and a glass-sealed iron piston which is moved up and down by a magnet. Stainless steel spiral springs were placed above and below the piston to prevent possible damage to the glass. The vertical cylinder, in which the level of mercury was set to the required height, had an inside diameter of 4.4 cm and was approximately 70 cm long. It served as a gas mixer and kept the pressure inside the circulating system constant by decreasing its volume when sample was taken. The circulating system with the exception of reaction vessel R and trap T, or the part enclosed by broken lines in Fig. 1, is hereinafter referred to as circulating system Sc, and the system “Sc+R” as reaction system Sr. When the mercury level in the cylinder was set to the lowest marker, the volume of the circulating system Sc was 2123 cc. The apparent volume*1 of R including the volume of stopcocks C_1 and C_3 was estimated to be 134 cc at reaction temperatures of 305 and 340°C. Most of the reaction vessel was made of quartz and hard glass as is illustrated in the scale drawing in Fig. 2. The rest of the circulating system was made of soft glass. The flow meter consisted of a constricted tube and a differential manometer containing high vacuum oil, and it was calibrated to a soap film meter with a 3:1 hydrogen-nitrogen mixture at several different pressures.

The circulating system was attached to a N^15H_3-dosing device, an analyzing system, etc., respectively through a stopcock. Fig. 3 illustrates the N^15H_3-dosing device which has a gas burette B_1 and a N^15H_3 reservoir. The gas burette could be separated into two parts, one of them having a manometer, by closing stopcock C_4. When the mercury level in the left arm of the monometer reached marker L, B_1 contained 26.8 or 67.4 cc depending upon whether stopcock C_4 was closed or open. Fig. 4 illustrates the analyzing system with gas pipettes GP_1 and GP_2, two traps

*) Let a reaction vessel be kept at a reaction temperature and be filled with gas at pressure P. The apparent volume of the reaction vessel is defined as the volume of gas which would result when the gas was cooled from the reaction temperature to a room temperature of 23°C at the same pressure P.
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in series, gas burette $B_2$, sample vessels $SV_1$ for nitrogen and $SV_2$ for ammonia. The volumes of the gas pipettes were 95.4 (GP$_1$) and 108.9 cc (GP$_2$). The gas burette $B_2$ was of the same type as $B_1$ of the $\text{N}^{15}\text{H}_2$-dosing device and had a volume of 2.71 or 8.73 cc.

2.2. Materials. The singly-promoted iron catalyst used to determine $\nu$, $\phi$ and $\psi$ was kindly provided by Dr. C. BOKHOVEN, the Netherlands, in the form of small granules.
This was a different portion of the same preparation (containing 0.88% Al₂O₃) as used by BOKHOVEN and his coworkers. The granules were crushed in a mortar and sieved, and 1.51 g of 30 to 40 mesh was charged to the reaction vessel R, as is shown in Figs. 1 and 2. It was then reduced in circulating hydrogen at a pressure of 400 to 580 mmHg for 72 hours at 450°C. The water vapor which was formed was removed through liquid nitrogen trap T, Fig. 1. The flow rate of hydrogen was 400 to 600 cc/min. Hydrogen consumption occurred in the initial few hours of the reduction, but after that time the manometer indicated no further consumption. From the amount of hydrogen consumed, it was calculated that the catalyst was reduced completely (100%) on a basis of 99% Fe₂O₃ and 1% unreducible promotors, but a lower value (92%) was obtained from the loss in weight of the catalyst during the reduction.

The hydrogen used to reduce the catalyst was prepared by electrolysis of concentrated potassium hydroxide, and was purified by passing it over platinum asbestos at 300 to 400°C and through two liquid nitrogen traps in series.

The 3:1 hydrogen-nitrogen mixture was prepared by catalyzed decomposition of ammonia as follows. Ammonia from a cylinder was condensed in a dry ice trap. The condensation was distilled in a vacuum at a temperature slightly higher than the dry ice temperature. The initial and final distillates were discarded and the remainder, about two thirds, was collected in another trap which was immersed in a dry ice bath. The ammonia thus purified was then passed slowly over a doubly promoted iron catalyst at a temperature of 500 to 600°C. The catalyst was charged to a different reactor than that used to determine $r$, $p$, and $\phi$. The 3:1 hydrogen-nitrogen mixture formed was passed through two liquid nitrogen traps in series to remove the undecomposed ammonia.

The $^{15}$N-enriched ammonia was prepared by gently heating a powdered mixture of $^{15}$N-enriched ammonium sulfate (0.5 g) and quick lime (1 g) in a vacuum. The resulting ammonia was dried by passing it over potassium hydroxide, then collected in a dry ice trap and fractionally distilled several times in a vacuum. The $^{15}$N-enriched ammonium sulfate was purchased from Rikagaku Kenkyusho (The Institute of Physical and Chemical Research), Tokyo. It was stated to be 99 $^{15}$N-atOMIC percent.

2.3. General Procedures. The singly-promoted iron catalyst charged to the reaction vessel R was reduced as described in the last section 2.2, and then evacuated for three hours at 400°C. A 3:1 hydrogen-nitrogen mixture was admitted to circulating system Sc with the exception of U-tube U. $^{15}$N-enriched ammonia was first admitted to gas burette B₁ of the $^{15}$H₂-dosing device where its pressure was determined, and then transferred to U by means of liquid nitrogen. Stopcock C₁ was closed and U was warmed to a room temperature, and the evaporated $^{15}$N-enriched ammonia and the 3:1 hydrogen-nitrogen mixture was circulated through by-pass stopcocks C₂ and C₄. The pressure of the resulting mixture (H₂+N₂+$^{15}$H₂), which was read by manometer M in circulating system Sc, was somewhat higher than 550 mmHg. At appropriate intervals during this circulation the resulting mixture was admitted to gas pipette GP₁ or GP₁+GP₂ and analyzed for ammonia. From these analyses, the partial pressure of ammonia in circulating system Sc were determined as is described in the next
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Section 2.4. The gas admitted into the gas pipette was further analyzed in a mass spectrometer for \( \text{N}^1\text{H}_3 \), \( \text{N}^\text{14}\text{N}'5 \) and \( \text{N}'5\text{N}'5 \) in order to determine \( Z_A \), \( Z_N \) and \( Z^* \). Details of these analytical procedures are also given in the next section. While the mixture was circulated as has been described above, the reaction vessel \( R \) was heated to a reaction temperature. Ammonia synthesis or decomposition was begun by switching the circulation from by-pass stopcock \( C_2 \) to reaction vessel \( R \), and simultaneously adjusting the total pressure to 550 mmHg. During the reaction, occasional samples were obtained by again admitting gas into gas pipette \( G_P \) or \( G_P_1+G_P_2 \) and analyzed to determine \( P_A \), \( Z_A \), \( Z_N \) and \( Z^* \). When these samples were taken, the volume of the reaction system was reduced by raising the mercury level in vertical cylinder \( V \) so as to keep the total pressure constant. Throughout the reaction, the total pressure and the catalyst temperature were thus controlled to within \( \pm 3 \) mmHg and \( \pm 1^\circ \text{C} \). The room temperature was set at \( 23 \pm 1^\circ \text{C} \). The reaction was continued until the changes in \( P_A \) became very slow or imperceptible. The reaction was terminated by closing stopcocks \( C_1 \) and \( C_3 \) and switching off the heater current to \( R \). In the following, the word “run” refers to the experimental procedures just described, from the admission of the 3:1 hydrogen-nitrogen mixture to system \( \text{Sc} - \text{U} \) to the termination of the reaction.

As are summarized in Table 2, seven successive runs (run 1 to run 7) were carried out over the same catalyst bed under various conditions. After run 7, the catalyst was withdrawn from reaction vessel \( R \). The materials in \( R \) other than the catalyst were treated with hydrogen as in the reduction of the catalyst but over a much shorter period of time 8 hours, and then evacuated for 3 hours at 400\(^\circ\text{C}\). Runs 8 to 10 were thus performed without the catalyst in order to examine whether the walls of \( R \) or the charged materials other than

<table>
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<th>Decomposition or synthesis</th>
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<th>Pressure [mmHg]</th>
<th>Reaction time [hrs]</th>
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<td></td>
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<tr>
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<td>1.9</td>
</tr>
<tr>
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<td>&quot;</td>
<td>(dec)</td>
<td>&quot;</td>
<td>&quot;</td>
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<td>7.0</td>
</tr>
<tr>
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<td>&quot;</td>
<td>(syn)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*) The catalyst was withdrawn after the reaction vessel was cooled to a room temperature and filled with ammonia to atmospheric pressure to prevent violent oxidation. The weight of catalyst withdrawn was 1.13 g.
the catalyst were catalytically active.

The stopcocks other than C₁ and C₃ were regreased before each run. In order to remove gases evolved from the grease, all of the apparatus with the exception of reaction vessel R was evacuated prior to each run until the residual pressure on standing overnight was \( 3 \times 10^{-3} \) mmHg or less. This was followed by the evacuation of R for 3 hours at 400°C.

2.4. Analytical Procedures. The gas mixture admitted to gas pipette GP₁ or GP₁+GP₂ was analyzed for total ammonia, \( \text{N}^\text{15}\text{H}_3 \), \( \text{N}^\text{14}\text{N}^\text{15} \) and \( \text{N}^\text{14}\text{N}^\text{18} \) as follows. The traps of the analyzing system were chilled by liquid nitrogen. The mixture in the gas pipette was slowly expanded through the traps into one of sample vessels SV₁ and the remainder was slowly pumped out. The ammonia frozen out in the traps was evaporated, transferred to gas burette B₂, and its pressure was read. The partial pressure \( P_{\text{A,obs.}} \) of ammonia in circulating system Sc or the partial pressure \( P_{\text{A}} \) of ammonia in reaction system Sr was determined from this pressure read and the volume ratio of GP₁ or GP₁+GP₂ to B₂ using BOYLE’s law. Before the reaction was begun, the total pressure of the gas mixture in Sc was somewhat higher than 550 mmHg as has been described in section 2.3. The values for \( P_{\text{A}} \) at \( t=0 \), i.e. at the beginning of the reaction, was therefore taken as 550 \( P_{\text{A,obs.}}/P_{T(0)} \) (mmHg), where the average of several measurements was used for \( P_{\text{A,obs.}} \), and \( P_{T(0)} \) was the total pressure of the gas mixture in Sc at \( t=0 \). The partial pressures \( P_{\text{H}} \) and \( P_{\text{N}} \) were taken as \( P_{\text{H}}=\frac{1}{4}(550-P_{\text{A}}) \) and \( P_{\text{N}}=\frac{1}{4}(550-P_{\text{A}}) \) (mmHg) respectively.

The ammonia in gas burette B₂ was then transferred to one of sample vessels SV₂ for mass spectrometric analysis to determine \( Z^\text{A} \). The analysis was kindly carried out by Prof. K. MIYAHARA with a mass spectrometer, which he constructed, by applying an electron accelerating voltage of 60 to 80 V. The ratio of peaks at \( m/e \) 18 to 17 was taken as the ratio of \( \text{N}^\text{15}\text{H}_3 \) to \( \text{N}^\text{14}\text{H}_3 \) after the contribution to \( m/e \) 18 by the \( \text{N}^\text{14}\text{H}_3^+ \) ion and to \( m/e \) 17 by the \( \text{N}^\text{15}\text{H}_3^+ \) ion were corrected.

The mixture of hydrogen and nitrogen admitted to SV₁ was analyzed for \( \text{N}^\text{14}\text{N}^\text{18} \) and \( \text{N}^\text{18}\text{N}^\text{15} \) in a Hitachi RMU-5B mass spectrometer in the Hitachi Central Research Laboratory, Hitachi Co., Ltd. Three peaks at \( m/e \) 28, 29 and 30 were measured at an electron accelerating voltage of 80 V. In the presence of hydrogen the observed ratio of peaks at \( m/e \) 29 to 28 appeared to increase linearly with increasing sample pressure \( P \) in the ionization chamber, although the ratio at 30 to 28 was nearly constant independent of the pressure. The linear increase can be accounted for by assuming the formation of the triatomic ion \( \text{N}^\text{14}\text{N}^\text{14}\text{H}^+ \) through a mechanism, e.g. \( \text{N}_2^+\text{H} \longrightarrow \text{N}_2\text{H}^++\text{H} \). It follows from this mechanism that the contribution to \( m/e \) 29 by the \( \text{N}^\text{14}\text{N}^\text{14}\text{H}^+ \) ion is proportional to \( P^2 \). On the other hand, the contribution to \( m/e \) 29 by the \( \text{N}^\text{14}\text{N}^\text{14}\text{H}^+ \) ion as well as the contribution to \( m/e \) 28 by \( \text{N}^\text{14}\text{N}^\text{14}\text{H}^+ \) ion appears proportional to \( P \).

Then, the ratio \( m/e \) 29 to 28 increases linearly with \( P \) as was actually observed, and the ratio \( \text{N}^\text{14}\text{N}^\text{15} \) to \( \text{N}^\text{14}\text{N}^\text{14} \) is taken as the limit approached by the ratio \( m/e \) 29 to 28 as \( P \) approaches zero. Thus, the procedure for determining the ratio \( \text{N}^\text{14}\text{N}^\text{15} \) to \( \text{N}^\text{14}\text{N}^\text{14} \) was to plot the observed \( m/e \) 29 to 28 ratio against \( P \) and to read the \( m/e \) ratio at \( P=0 \) by extrapolation of the straight line plot obtained. This procedure was examined in a separate experiment by analyzing a 3:1 hydrogen-ordinary nitrogen mixture. The observed \( \text{N}^\text{14}\text{N}^\text{18} \) to \( \text{N}^\text{14}\text{N}^\text{14} \) ratio was 0.00721 as compared with the theoretical value 0.00729, which was derived from the natural abundance.

*) This mass spectrometer was designated in reference (4) as “mass spectrometer II".
0.365% of N\textsuperscript{15} and the equilibrium constant 4 for the nitrogen isotopes equilibration, \textit{N}\textsuperscript{14}N\textsuperscript{15} + N\textsuperscript{14}N\textsuperscript{15} = 2N\textsuperscript{14}N\textsuperscript{15}. This close agreement gives considerable confidence to the above procedure for determining the N\textsuperscript{14}N\textsuperscript{15} to N\textsuperscript{14}N\textsuperscript{15} ratio. On the other hand, the m/e 30 to 28 ratios measured at various \textit{P} were averaged, and the mean value was taken as the ratio of N\textsuperscript{15}N\textsuperscript{15} to N\textsuperscript{14}N\textsuperscript{15}.

3. Results and Discussion

3.1. Manometric and Mass Spectrometric Analyses. Tables 3a to 3h summarize the results of runs 3 to 10 respectively. The data from runs 1 and 2 were omitted as they were inaccurate. As has been previously described (section 2.3), samples were also taken at appropriate intervals during each run before the reaction vessel \textit{R} was opened, \textit{i.e.} at reaction time \textit{t}=0. These samples are designated as \textit{O}_a, \textit{O}_b, \textit{O}_c, etc., in order of sampling, and generically as “\textit{O}”. In Table 4, the values for \textit{P}_{\textit{A,obs.}} are listed for each of these samples \textit{O}.

As may be seen from Tables 2 and 3, in each run, \textit{P}_A was negligibly small in comparison with the total pressure, 550 mmHg. In consequence, the volume \textit{V}_t of reaction system \textit{S}_R needed not be varied in order to keep the total pressure constant during the period of time between any two successive samplings, although \textit{V}_t decreased stepwise every time a sample was taken, as is shown in Tables 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>\textit{t} (hr.)</th>
<th>\textit{V}_t (cc)</th>
<th>\textit{P}_A (mmHg)</th>
<th>\textit{Z}_A</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>2258</td>
<td>1.96</td>
<td>0.961</td>
</tr>
<tr>
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<td>0.3</td>
<td>2072</td>
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<td>0.816</td>
</tr>
<tr>
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<td>5.0</td>
<td>1864</td>
<td>2.36</td>
<td>0.723</td>
</tr>
<tr>
<td>3</td>
<td>13.8</td>
<td>1766</td>
<td>2.68</td>
<td>0.567</td>
</tr>
<tr>
<td>4</td>
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<td>1669</td>
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</tr>
<tr>
<td>5</td>
<td>37.8</td>
<td>1578</td>
<td>3.32</td>
<td>0.360</td>
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<tr>
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<td>1486</td>
<td>3.59</td>
<td>0.266</td>
</tr>
<tr>
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<td>1386</td>
<td>3.67</td>
<td>0.194</td>
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<td>101.8</td>
<td>1288</td>
<td>3.78</td>
<td>0.126</td>
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<tr>
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<td>123.8</td>
<td>1188</td>
<td>3.80</td>
<td>0.129</td>
</tr>
</tbody>
</table>

\textit{t}, reaction time; \textit{V}_t, volume of reaction system \textit{S}_R (reaction vessel \textit{R} + space enclosed by broken lines in Fig. 1) during the interval between two successive samplings; \textit{P}_A, partial pressure of ammonia in reaction system \textit{S}_R; \textit{Z}_A, N\textsuperscript{15}-atomic fraction of ammonia.
### Table 3b. Run 4. Ammonia decomposition and N\textsuperscript{15}-exchange between ammonia and nitrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( t ) (hr.)</th>
<th>( V_t ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A )</th>
<th>( Z^N )</th>
<th>( Z_{1}^N )</th>
<th>( Z_{1}^N )</th>
<th>( Z_{1}^N )</th>
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</thead>
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<td></td>
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<td>0.0322</td>
<td>0.0171</td>
<td>0.0332</td>
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</tr>
</tbody>
</table>

\( Z^N \), mole fraction of N\textsuperscript{14}N\textsuperscript{15} in nitrogen; \( Z_{1}^N \), mole fraction of N\textsuperscript{14}N\textsuperscript{18} in nitrogen; \( Z_{1}^N \), N\textsuperscript{15} atomic fraction of nitrogen.

### Table 3c. Run 5. Ammonia synthesis and N\textsuperscript{15}-exchange between ammonia and nitrogen.

<table>
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<th>Sample</th>
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<th>( V_t ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A )</th>
<th>( Z^N )</th>
<th>( Z_{1}^N )</th>
<th>( Z_{1}^N )</th>
<th>( Z_{1}^N )</th>
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<td>0.0002</td>
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The Rate-Determining Step of Ammonia Synthesis and Decomposition Part 1.

### TABLE 3d. Run 6. Ammonia decomposition and N¹⁵-exchange between ammonia and nitrogen.

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<tr>
<th>Sample</th>
<th>( t ) (hr.)</th>
<th>( V_i ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z )</th>
<th>( Z^{-1} )</th>
<th>( Z^{N} )</th>
<th>( Z^{N} )</th>
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### TABLE 3e. Run 7. Ammonia synthesis and N¹⁵-exchange between ammonia and nitrogen.

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<th>( V_i ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z )</th>
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</tr>
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</tr>
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<td>3.71</td>
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TABLE 3f. Run 8. Blank run without catalyst.

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<th>( V_t ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A )</th>
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</thead>
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</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>2115</td>
<td>1.83</td>
<td>0.905</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>2020</td>
<td>1.72</td>
<td>0.904</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>1920</td>
<td>1.83</td>
<td>0.897</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>1832</td>
<td>1.87</td>
<td>0.904</td>
</tr>
<tr>
<td>5</td>
<td>22.0</td>
<td>1739</td>
<td>1.88</td>
<td>0.920</td>
</tr>
<tr>
<td>6</td>
<td>26.0</td>
<td></td>
<td>1.87</td>
<td>0.902</td>
</tr>
</tbody>
</table>

TABLE 3g. Run 9. Blank run without catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( t ) (hr.)</th>
<th>( V_t ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2252</td>
<td>7.10</td>
<td>0.937</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>2161</td>
<td>7.04</td>
<td>0.944</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>2065</td>
<td>6.93</td>
<td>0.951</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>1963</td>
<td>7.03</td>
<td>0.951</td>
</tr>
<tr>
<td>4</td>
<td>11.0</td>
<td>1869</td>
<td>6.98</td>
<td>0.949</td>
</tr>
<tr>
<td>5</td>
<td>19.0</td>
<td>1775</td>
<td>6.99</td>
<td>0.953</td>
</tr>
<tr>
<td>6</td>
<td>30.0</td>
<td></td>
<td>6.95</td>
<td>0.953</td>
</tr>
</tbody>
</table>

TABLE 3h. Run 10. Blank run without catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( t ) (hr.)</th>
<th>( V_t ) (cc)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2197</td>
<td>1.68</td>
<td>0.936</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>1995</td>
<td>1.67</td>
<td>0.938</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>1791</td>
<td>1.74</td>
<td>0.935</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td></td>
<td>1.73</td>
<td>0.938</td>
</tr>
</tbody>
</table>
The Rate-Determining Step of Ammonia Synthesis and Decomposition Part 1.

**TABLE 4.** Adsorption of ammonia on the apparatus.
A comparison between the calculated and observed pressures of ammonia admitted to circulating system $S_C$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Time (hr.)</th>
<th>$V'_f$ (cc)</th>
<th>$P_T$ (mmHg)</th>
<th>$P_{A,calc}$ (mmHg)</th>
<th>$P_{A,obs}$ (mmHg)</th>
<th>$P_{AG}$ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$O_a$</td>
<td>1.0</td>
<td>615</td>
<td>2.54</td>
<td>2.20</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>8.1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.18</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$O_a$</td>
<td>1.0</td>
<td>621</td>
<td>9.31</td>
<td>9.00</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>5.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>8.99</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$O_a$</td>
<td>1.0</td>
<td>609</td>
<td>4.42</td>
<td>4.08</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>4.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4.13</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$O_a$</td>
<td>1.0</td>
<td>614</td>
<td>13.63</td>
<td>13.26</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>4.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>13.27</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$O_a$</td>
<td>1.0</td>
<td>607</td>
<td>2.57</td>
<td>2.31</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>5.3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.36</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_c$</td>
<td>24.7</td>
<td>2023</td>
<td>&quot;</td>
<td>2.33</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$O_a$</td>
<td>0.5</td>
<td>597</td>
<td>2.40</td>
<td>2.09</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>3.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.14</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$O_a$</td>
<td>0.5</td>
<td>652</td>
<td>8.80</td>
<td>8.43</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>3.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>8.46</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_c$</td>
<td>20.0</td>
<td>2040</td>
<td>&quot;</td>
<td>8.36</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$O_a$</td>
<td>3.0</td>
<td>696</td>
<td>2.42</td>
<td>2.14</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_b$</td>
<td>24.1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.12</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_c$</td>
<td>115.3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.08</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_d$</td>
<td>167.2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.12</td>
<td>0.30</td>
<td></td>
</tr>
</tbody>
</table>

Mean 0.32

Sample has been defined on page 131. Time is the time allowed for the mixture of $H_2$, $N_2$, and $^{15}N_H$, to circulate or to stand in circulating system $S_C$. The mixture was circulated constantly for the first several hours, and intermittently following them. $V'_f$ is the volume of circulating system $S_C$ during the interval between two successive samplings. $P_T$ is the total pressure of the mixture when sampled. $P_{A,calc}$ and $P_{A,obs}$ have been defined in sections 3.3 and 2.4 respectively. $P_{AG}$ is the difference between $P_{A,calc}$ and $P_{A,obs}$, i.e. $P_{AG} = P_{A,calc} - P_{A,obs}$. 
Table 5. Mass spectrometric analysis of a series of ammonia samples in run 6 to determine memory effect.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Z^A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oa</td>
<td>0.980</td>
</tr>
<tr>
<td>Ob</td>
<td>(0.938)</td>
</tr>
<tr>
<td>1</td>
<td>0.942</td>
</tr>
<tr>
<td>2</td>
<td>0.925</td>
</tr>
<tr>
<td>3</td>
<td>0.928</td>
</tr>
<tr>
<td>4</td>
<td>0.898</td>
</tr>
<tr>
<td>5</td>
<td>0.883</td>
</tr>
<tr>
<td>6</td>
<td>0.847</td>
</tr>
<tr>
<td>7</td>
<td>0.778</td>
</tr>
<tr>
<td>8</td>
<td>0.738</td>
</tr>
<tr>
<td>9</td>
<td>0.672</td>
</tr>
<tr>
<td>10</td>
<td>0.587</td>
</tr>
<tr>
<td>11</td>
<td>0.496</td>
</tr>
<tr>
<td>12</td>
<td>0.405</td>
</tr>
</tbody>
</table>

Arrow shows order of measurements.

Ammonia tends to be strongly adsorbed on the walls of the mass spectrometer, thus giving rise to a considerable memory effect, which makes accurate analysis very difficult. In order to minimize this memory effect, each sample of ammonia was allowed to leak into the mass spectrometer for about 10 minutes prior to being measured, and in run 6 the memory effect was examined by analyzing some of the ammonia samples two or three times as is shown in Table 5. The results appear to indicate that in these experiments the memory effect was not very serious. The Z^A values measured for the same sample agreed within 3% with the exception of the value in parentheses. In Table 3 d, the Z^A values given for each sample are mean values of those given in Table 5. In comparison with the N^15-atomic fraction (0.99) of ammonium sulfate from which the N^15-enriched ammonia was made, the Z^A values for samples O varied from run to run and were appreciably lower, ranging from 0.976 (run 6) to 0.824 (run 7). The source of this fluctuation and dilution is not clear, however.

3.2. Equilibrium Constant and Heat of Reaction. In Figs. 5 a, 5 b and 5 c, P_A is plotted against t for each run. From these figures, (P_A)_{0}, the partial pressure of ammonia in equilibrium may be estimated as 3.8 mmHg at
340°C and 7.0 mmHg at 305°C*). It is calculated using these \((P_A)_{e}\) values that the equilibrium constant \(K_s\) of ammonia synthesis (1) is \(1.54 \times 10^{-8}\) and \(5.34 \times 10^{-9}\) mmHg\(^{-2}\) at the respective temperatures and that the heat of reaction, \(Q_p\), is 25.1 Kcal per mole. These values are now compared with those calculated from HABER's formula,

\[
\log K_s = 2 \times \{2.098.2/T - 2.509 \log T - 1.006 \times 10^{-4} T + 1.860 \times 10^{-7} T^2 + 2.10\},
\]

i.e. \(2.05 \times 10^{-9}\) mmHg\(^{-2}\) at 340°C, \(6.99 \times 10^{-9}\) mmHg\(^{-2}\) at 305°C, and 24.7 Kcal. It may be seen that for \(Q_p\) the results of the present work agree closely with those obtained by HABER, but are appreciably lower than his for \(K_s\). Using HABER's formula, the values for \((P_A)_{e}\) are 4.38 mmHg

---

* In each run, the derivative \(dP_A/dt\) was discontinuous each time a sample was taken because of a stepped decrease in the volume of the reaction system. In Figs. 5a and 5b, the smoothed broken lines, therefore, do not exactly fit the actual \(P_A\) vs. \(t\) curves. This deviation should tend to vanish as the equilibrium is approached, so that it would make hardly any difference in the determination of \((P_A)_{e}\). The discontinuity will be discussed in more detail in the future.
Fig. 5 b. The pressure of ammonia plotted against time at 305°C. Arrow shows the pressure of ammonia in equilibrium as derived by HABER's equilibrium constant.

Fig. 5 c. The pressure of ammonia plotted against time in blank runs (340°C).
at 340°C and 7.98 mmHg at 305°C under the conditions of the present work. ENOMOTO and HORIUTI also reported a \((P_A)_e\) value which was appreciably lower than would have been expected from HABER's formula.

3.3. **Adsorption of Ammonia.** As was described in section 2.3, at the beginning of each run, a measured amount of N\textsuperscript{15}-enriched ammonia was admitted from gas burette B, to circulating system S\textsubscript{c}, mixed with 3:1-hydrogen and nitrogen mixture. Therefore, using BOYLE's law we can calculate the partial pressure of the ammonia in S\textsubscript{c} from the volumes of B\textsubscript{1} and S\textsubscript{c} and the pressure determined in B\textsubscript{1}. The values thus calculated, \(P_{A,\text{calculated}}\), are compared with \(P_{A,\text{observed}}\) in Table 4. The difference, \(P_{A,\text{calculated}} - P_{A,\text{observed}}\), is attributable to the adsorption of ammonia in the apparatus, presumably on the glass walls. The amount of the adsorption appears independent of the pressure of ammonia over the range observed, \(i.e.\) 2 to 13 mmHg. Table 4 also indicates that the adsorption is so rapid that adsorption equilibrium is established within 0.5 hour at most.

A subsidiary experiment was conducted to confirm the adsorption of ammonia in the apparatus in the following way. Gas burette B\textsubscript{1} connected with gas reservoir D was filled with nitrogen and the pressure was read with the manometer of B\textsubscript{1}. The nitrogen was then allowed to expand into both circulating system S\textsubscript{c} and Mcleod gauge E temporarily attached to S\textsubscript{c} for this subsidiary experiment, and the pressure was read with E. There seemed to be no indication that after expansion the pressure varied with time. After thorough evacuation the same procedure was repeated using nearly the same amount of

**Table 6.** Subsidiary experiment in confirmation of the adsorption of ammonia in the apparatus. Comparison between the pressures of nitrogen and ammonia individually admitted to circulating system S\textsubscript{c} and communicating part.

<table>
<thead>
<tr>
<th>Part of the apparatus containing N\textsubscript{2} or N\textsuperscript{15}H\textsubscript{3}</th>
<th>N\textsubscript{2} admitted</th>
<th>N\textsuperscript{15}H\textsubscript{3} admitted</th>
<th>(P_{N_2}\times\frac{48.87}{49.89} - P_{N^{15}\text{H}_3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{1}+D</td>
<td>48.87</td>
<td>49.89</td>
<td>0.00</td>
</tr>
<tr>
<td>B\textsubscript{1}+D+S\textsubscript{c}+E</td>
<td>12</td>
<td>2.50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.50</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>2.50</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2760</td>
<td>2.19</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3960</td>
<td>2.18</td>
<td>20</td>
</tr>
</tbody>
</table>

D: gas reservoir attached to gas burette B\textsubscript{1}.
E: Mcleod gauge temporarily attached to circulating system S\textsubscript{c}.
Time: time elapsed following expansion of N\textsubscript{2} or N\textsuperscript{15}H\textsubscript{3} into space B\textsubscript{1}+D+S\textsubscript{c}+E.
Kazunori Tanaka

N\textsuperscript{15}-enriched ammonia instead of nitrogen. In this case the pressure measured by E decreased very slowly over a long period of time as is shown in Table 6. In this Table, the last column \((49.89 P_{N/48.87}) - P_{N15H}\) is the difference between the pressures of nitrogen and N\textsuperscript{15}-enriched ammonia which would have resulted had the same amount of nitrogen and N\textsuperscript{15}-enriched ammonia been used. The differences are hence attributable to the adsorption of ammonia in the apparatus and they are in fair agreement with the adsorption previously estimated, \((P_{A,\text{calc.}} - P_{A,\text{obs.}}, \text{Table 4})\). This subsidiary experiment also showed that the initial rapid adsorption of ammonia, which was completed within 5 minutes at most, was followed by very slow adsorption. However, in no case was such slow adsorption observed in the experiment summarized in Table 4. This different behavior remains to be elucidated, but it appears to be explained by the difference in experimental conditions since the experiment in Table 4 involved hydrogen and nitrogen as well as ammonia, whereas only ammonia was involved in the subsidiary experiment.

It is now possible to estimate the coverage of the ammonia adsorbed on the assumption that the adsorption occurred solely on the glass walls of the apparatus. As is shown in Table 4, the mean value for \(P_{A,0}\), i.e. the decrease in pressure of ammonia resulting from adsorption on the glass walls of circulating system \(S_{C}\), was 0.32 mmHg. This corresponds to 37 \(\mu\)moles or \(2.2 \times 10^{19}\) molecules taking the volume of \(S_{C}\) as 2123 cc. The inner surface area \(S\) of \(S_{C}\) was estimated roughly as

\[
S = 4100 f_1 + 150 f_2 \quad (\text{cm}^2)
\]

by measuring the lengths and diameters of the component parts of the glass tubes, where \(f_1\) and \(f_2\) are the roughness factors of smooth and ground glass walls respectively. Putting \(f_1\) and \(f_2\) as 1 and 2 respectively and assuming the cross-sectional area of an ammonia molecule to be 12.6 \(\text{Å}^2\),\textsuperscript{7} the coverage is calculated to be about 6 molecular layers. The adsorption of ammonia on glass has also been observed by other investigators. According to Francis and Burt,\textsuperscript{8} the adsorption of ammonia on glass wool extended to 12 molecular layers at 0°C and one atmosphere. Evans and George\textsuperscript{9} reported even greater adsorption, 23 molecular layers at the same temperature on the same material but at much lower pressure of 74 mmHg. Wahba and Kemball\textsuperscript{10} found \(1-6 \times 10^{17}\) molecules of ammonia to be adsorbed on the walls of McLeod gauge and connecting tubing at 21°C over a pressure range of \(10^{-3} \sim 10^{-1}\) mmHg.

As is evident in Figs. 5a and 5b, the pressure \(P_A\) of ammonia dropped very rapidly at the beginning of ammonia synthesis and decomposition, and
then slowly increased or decreased respectively toward equilibrium pressure. A similar rapid decrease in the initial stage was also observed in the $N^{15}$-atomic fraction $Z_A$ of ammonia as is exemplified in Fig. 6. Tables 3f to 3h and Fig. 5c, however, show that these rapid decreases in both $P_A$ and $Z_A$ did not occur in blank runs 8, 9 and 10 where the reaction vessel did not contain the catalyst. The rapid decrease in $P_A$ is therefore attributable to the rapid adsorption of ammonia on the catalyst. On the assumption that this rapid adsorption was completed just prior to the time when sample 1 was taken, the number of moles $a_c$ of ammonia adsorbed on the catalyst can be calculated for each run from

$$a_c = P_{Ac} V_d/RT,$$

where $P_{Ac}$ is the difference in $P_A$ value between samples 0 and 1. Putting $T$ as 296°K and $V_d$ as the constant value during the interval between samples 0 and 1 as listed in Tables 3, the calculated values of $a_c$ are shown in Table 7.

![Fig. 6. Typical rapid drop in $Z_A$ in the initial stage of the reaction.](image)

### Table 7. Adsorbed ammonia and residual nitrogen on the catalyst.

<table>
<thead>
<tr>
<th>Run</th>
<th>Syn. or decompn.</th>
<th>Temp. ($^\circ$C)</th>
<th>$P_A$ of Sample 1 (mmHg)</th>
<th>$a_c$ (μmole)</th>
<th>$n_R$ (μmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Syn.</td>
<td>340</td>
<td>1.73</td>
<td>28</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>decompn.</td>
<td>n</td>
<td>7.45</td>
<td>63</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>Syn.</td>
<td>305</td>
<td>3.39</td>
<td>39</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>decompn.</td>
<td>n</td>
<td>11.44</td>
<td>55</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>Syn.</td>
<td>340</td>
<td>1.92</td>
<td>22</td>
<td>—</td>
</tr>
</tbody>
</table>

*mean* 51

$a_c$; the number of moles of ammonia rapidly adsorbed on the catalyst at the beginning of the reaction.

$n_R$; the number of moles of residual nitrogen left on the catalyst after evacuation for 3 hours at 400°C.
When the catalyst was evacuated for 3 hours at 400°C prior to each run, desorption of gas from the catalyst was observed by McLeod gauge even at the end of the evacuation, suggesting that an appreciable amount of nitrogen was left on the catalyst in some form. The N\textsuperscript{15}-atomic fraction \( Z^{N(R)} \) of this residual nitrogen would be close to zero rather than to unity, since normal nitrogen far surpassed N\textsuperscript{15}-enriched ammonia in pressure in the reaction mixture. The initial rapid drop in \( Z^A \) as exemplified in Fig. 6 is therefore attributable to a rapid exchange of N\textsuperscript{15}-atoms between the residual nitrogen and the N\textsuperscript{15}-enriched ammonia. Assuming that when sample 1 was taken, N\textsuperscript{15}-atoms were evenly distributed among the residual nitrogen, gaseous ammonia and adsorbed ammonia, and neglecting the transfer of N\textsuperscript{15}-atoms to gaseous nitrogen, we have

\[
Z^A_0 (a_{(1)} + a_g + a_C) + Z^{N(R)} n_R = Z^A_1 (a_{(1)} + a_g + a_C + n_R),
\]

where \( a_g \) is the number of moles of ammonia adsorbed on the glass walls of circulating system \( S_C \), \( n_R \) is the number of moles of the residual nitrogen, and subscripts (0) and (1) specify the quantities just before samples 0 and 1 are taken respectively. We have from Eq. (21)

\[
n_R = (a_{(1)} + a_g + a_C) \frac{Z^A_0 - Z^A_1}{Z^A_1 - Z^{N(R)}},
\]

The \( Z^{N(R)} \) value not actually measured may be identified with the average value 0.03 of \( Z_t \), which lies in a range of 0.014 to 0.045 as will be described in the next section 3.4. Using Eq. (22), the \( n_R \) values were calculated for each run with the exception of run 7, where no rapid initial drop in \( Z^A \) was distinctly observed. The calculated values of \( n_R \) are given in Table 7. It may be seen that they agree closely with one another. These results appear reasonable since evacuation of the catalyst was carried out under the same conditions prior to each run, i.e. for 3 hours at 400°C.

### 3.4. Balance of N\textsuperscript{15}

For most samples in runs 4, 5 and 6, \( Z^N \) as well as \( Z^A \) was measured with the mass spectrometer. By calculating \( Z_t \) from Eq. (11.b) the N\textsuperscript{15}-balance throughout a single run may hence be checked with these samples as well as with sample 0. In this calculation, the \( Z^N \) value for samples 0 was taken as 0.00365 or the generally accepted natural abundance of N\textsuperscript{15}, as mass spectrometric determination of \( Z^N \) was unsuccessful for these samples. As is shown in Table 8, the \( Z_t \) value thus calculated appears to decrease rapidly in the early stage of the reaction and then slowly increase.

\*\*\*  \( a_{(1)} = P_0 V_{(0-1)} / RT \), where \( V_{(0-1)} \) is the value of \( V_t \) in liter during the interval between samples 0 and 1.

\*\*\*  \( a_{(1)} = P_0 V_{(0-1)} / RT \),
It should be noted that Eq. (11. b) is based upon the tacit assumption that neither ammonia nor nitrogen is adsorbed. The initial rapid decrease in \( Z_i \) is thus ascribed to the adsorption of ammonia on the catalyst and to the exchange of \( \text{N}^{15} \)-atoms between the ammonia and the residual nitrogen as was discussed in the preceding section. The later slow increase in \( Z_i \) is probably attributable to the gradual transfer of \( \text{N}^{15} \)-atoms from the adsorbed ammonia on the catalyst and glass walls to the gaseous ammonia and gaseous nitrogen.

The \( \text{N}^{15} \)-balance is now considered taking into account the adsorption discussed in the previous section. Defining \( Z' \) as the \( \text{N}^{15} \)-atomic fraction of gaseous ammonia, gaseous nitrogen, residual nitrogen, or ammonia adsorbed on the catalyst and glass walls in exchange equilibrium of \( \text{N}^{15} \) among them, we have

\[
Z' = \frac{Z'_{(0)}(a_{(0)} + a_{(0)} + a_{(0)} + n_{(0)} + 2n_{(0)})}{a_{(0)} + a_{(0)} + n_{(0)} + 2n_{(0)}}
\]

for sample 0 \( (23. \text{a}) \)

and

\[
Z'_{(i)} = \frac{Z'_{(i)}(a_{(i)} + a_{(i)} + a_{(i)} + n_{(i)} + 2n_{(i)})}{a_{(i)} + a_{(i)} + a_{(i)} + n_{(i)} + 2n_{(i)}}
\]

for sample \( i \) \( (i \geq 1) \), \( (23. \text{b}) \)

where the subscripts \( (0) \) and \( (i) \) specify the quantities just before samples 0 and \( i \) are taken respectively. Eq. (23.b) is based upon the assumption that the adsorbed ammonia and residual nitrogen are in isotopic equilibrium with the gaseous ammonia but not with the gaseous nitrogen. In calculating \( Z' \) from

![Fig. 7](image-url)
Eqs. (23.b), \( a_c \) and \( nR \) were taken as 37 and 51 \( \mu \)moles respectively (section 3.3). As is shown in Fig. 7, \( a_c \) appears to depend upon \( P_A \), but the data are insufficient to draw an accurate isotherm. Accordingly from Fig. 7, \( a_c \) was taken as the average value over the range of \( P_A \) of respective runs, i.e. 50, 45 and 60 \( \mu \)moles for runs 4, 5 and 6, respectively. The values of \( a_{(c)} \) and \( a_{(0)} \) were computed using the data in Tables 3.\(^{*)}\) The values of \( Z_i \) thus calculated are given together with \( Z_i \) in Table 8. It may be seen that \( Z_i \) is nearly constant throughout a single run, indicating that the manometric and mass spectrometric analyses are reliable.

### Table 8. The values for \( Z_i \) and \( Z_i' \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>( Z_i )</td>
<td>( Z_i' )</td>
<td>( Z_i )</td>
</tr>
<tr>
<td>0</td>
<td>0.0307</td>
<td>0.0317</td>
<td>0.0161</td>
</tr>
<tr>
<td>1</td>
<td>0.0277</td>
<td>0.0313</td>
<td>0.0141</td>
</tr>
<tr>
<td>2</td>
<td>0.0291</td>
<td>0.0326</td>
<td>0.0144</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.0159</td>
</tr>
<tr>
<td>4</td>
<td>0.0307</td>
<td>0.0334</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.0322</td>
<td>0.0337</td>
<td>0.0159</td>
</tr>
<tr>
<td>6</td>
<td>0.0321</td>
<td>0.0329</td>
<td>0.0159</td>
</tr>
<tr>
<td>7</td>
<td>0.0336</td>
<td>0.0340</td>
<td>0.0170</td>
</tr>
<tr>
<td>8</td>
<td>0.0332</td>
<td>0.0332</td>
<td>0.0170</td>
</tr>
<tr>
<td>9</td>
<td>0.0332</td>
<td>0.0332</td>
<td>0.0170</td>
</tr>
<tr>
<td>10</td>
<td>0.0332</td>
<td>0.0332</td>
<td>0.0170</td>
</tr>
<tr>
<td>11</td>
<td>0.0332</td>
<td>0.0332</td>
<td>0.0170</td>
</tr>
</tbody>
</table>

3.5. \( \nu_r \). In Fig. 8, the observed values of \( Z^A \) and \( Z^N \) with the exception of those for samples 0 are plotted against \( \log P_A \) for runs 3 to 7 (open circles and triangles). The value for \( Z_i \) at \( (P_A)_{(e)} \) is also plotted for each run (solid circles and triangles). Since a steady state condition of synthesis or decomposition was assumed in deriving Eqs. (8), (10) and (12) for evaluating \( \nu_r \), the values for samples 0 were omitted because such a steady state condition was not obtained during the interval between samples 0 and 1. The values of \( \nu_r \) calculated at various points on the \( Z^A \) vs. \( \log P_A \) or \( Z^N \) vs. \( \log P_A \) curves are plotted against chemical affinity or \( P_A \) in Figs. 9a and 9b, where Roman

\[ a_{(c)} = P_A V_{(i-1)} \ln P_A / RT, \]

where \( V_{(i-1)} \) is the value of \( V_i \) in liter during the interval between samples \( i-1 \) and \( i \). When \( i = 0 \), however, \( a_{(0)} = P_A (V_{(0)}+0.095) / RT \), where 0.095 is the volume in liter of gas pipette GP.
Fig. 8. Logarithm of $P_A$ (pressure of ammonia) against $Z^A$ (N$^{15}$-atomic fraction of ammonia) or $Z^N$ (N$^{15}$-atomic fraction of nitrogen).
numerals I and II correspond with those in Fig. 8. The calculations were not made at points very close to equilibrium because there a very small error in the $-\Delta F$ evaluation etc. would seriously affect the value for $v_r$.

In decomposition runs 4 and 6, the $v_r$ values calculated from Eq. (8) are very close to unity over the entire range of chemical affinity studied, indicating that the desorption of chemisorbed nitrogen or step (2,1) is rate-determining. In run 6, this is further confirmed by calculating $v_r$ from equation (10). The values obtained from the latter equation are also near unity although the devia-
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Fig. 9 b. Observed values for $\nu_r$, $\phi$ and $\psi$ at 305°C as a function of chemical affinity.

In synthesis run 5, the $\nu_r$ values calculated from Eq. (10) is near unity although in some regions they deviate considerably upwards. This indicates that the chemisorption of nitrogen or step (2.1) is rate-determining. In contrast, the $\nu_r$ values calculated from Eq. (8) are a little lower than unity ($\sim 0.7$) in a region near equilibrium, decrease with increasing chemical affinity to zero, and become meaningless at chemical affinities of over approximately 1500 cal, where the antilogarithmic part of the term $\ln[1/(1-(Z^n-Z^n)d\ln P_A/dZ^A)]$ is negative. The same tendency is seen with $\nu_r$ values calculated from Eq. (12).
for the other synthesis runs 3 and 7. Possible alteration in \( Z^A \) vs. \( \log P_A \) curve would not change this tendency as may be seen by comparison of curves I and II of run 3 in Figs. 8 and 9a.

This curious phenomenon appears to result from the adsorption of ammonia on both the catalyst and glass walls. Adsorption was not taken into account in any of the equations for evaluating \( \nu_r \). It should be remembered that the term \( d \ln P_A/dZ_A \) appears in Eqs. (8) and (12) while in Eq. (10) the term \( d \ln P_A/dZ^N \) is used instead. A future publication will show that the effect of the adsorption on \( \nu_r \) may be disclosed especially if Eq. (8) or (12) is used in the synthesis run, and that by correcting for the adsorption, \( \nu_r \) values of near unity will be obtained over the entire range of chemical affinity concerned even with synthesis runs 3, 5, and 7.

3.6. \( \phi \) and \( \phi \). The \( \phi \) values calculated from Eq. (13) taking \( K_N \) as 4 are plotted against chemical affinity in Figs. 9a and 9b for runs 4, 5 and 6. It may be seen that \( \phi \) is practically zero over most region of chemical affinity studied, providing additional evidence that step (2.1) is rate-determining.

![Fig. 10. \( Z^N \) and \( Z^A \) plotted against \( Z^N \) for runs 4 and 6.](image)

Fig. 10 shows the \( Z^N \) vs. \( Z^N \) and \( Z^N \) vs. \( Z^A \) curves for runs 4 and 6. At various \( Z^N \) values, the \( Z^A \) value and tangent \( dZ^A/dZ^N \) were read to calculate \( \phi \) using Eq. (16). The values calculated are plotted against chemical affinity in Figs. 9a and 9b. It may be seen that \( \phi \) is near unity over the entire region of chemical affinity studied, further verifying that step (2.1) is rate-determining.

3.7. Conclusion. From the values for \( \nu_r \), \( \phi \) and \( \phi \) observed, it may be
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unambiguously concluded that step (2.1), i.e. nitrogen chemisorption in ammonia synthesis and nitrogen desorption in ammonia decomposition, is rate-determining over a singly-promoted iron catalyst at 305 and 340°C near one atmosphere.

In reaching this conclusion as to the rate-determining step, the effect of diffusion has not been taken into account. It is considered briefly. If there were any diffusion effect in the present experiments, it should be diffusion of ammonia from catalyst surface to the surrounding gaseous stream or the reverse, since the pressures of hydrogen and nitrogen far surpassed that of ammonia. Two moles of ammonia appear in the overall reaction (1). Therefore, if the overall reaction rate were controlled by the diffusion process, the value for \( \nu \) would be 2. In addition, \( N(a) \) would be in partial equilibrium with gaseous nitrogen. The results actually obtained contradict these expectations, ruling out the diffusion effect.

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