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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 13(2), 119-150
Issue Date	1966-01
Doc URL	https://hdl.handle.net/2115/24798
Type	departmental bulletin paper
File Information	13(2)_P119-150.pdf

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 13, No. 2, pp. 119 to 150 (1965)

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

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(Received October 10, 1965)

Abstract

Kinetic investigation has been made of ammonia synthesis and decomposition using N^{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 ν_r (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 ν_r values were appreciably lower than unity and decreased to zero with increasing chemical affinity. It is preliminarily noticed that this peculiar behavior of ν_r can be explained as resulting from the observed adsorption 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-determining step in catalyzed ammonia synthesis and decomposition

$$3H_2+N_2=2NH_3 \tag{1}$$

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

$$N_2 \rightleftharpoons 2N(a) \qquad 1 \tag{2. I}$$

$$H_2 \rightleftharpoons 2H(a) \qquad 3 \tag{2. II}$$

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

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$$\left.\begin{array}{ll} N(a)+H(a) \rightleftharpoons NH(a) & 2 \\ NH(a)+H(a) \rightleftharpoons NH_2(a) & 2 \\ NH_2(a)+H(a) \rightleftharpoons NH_3\,, & 2 \end{array}\right\} \qquad (2.\text{III})$$

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 ν_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.[1] The observed ν_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 ν_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 ν_r and partial equilibrium can simultaneously be determined in a single experiment.

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 ν_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[2)]

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

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

$$-\Delta F = RT\ln\left(\frac{P_H^3 P_N}{P_A} K_S\right). \tag{4}$$

The overall reaction rate V may be written as

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

$$= -\frac{dn}{dt}, \tag{5. b}$$

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

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

or

$$\frac{d(Z^N n)}{dt} = Z^A V_- - Z^N V_+, \tag{6. b}$$

where Z^{A} and Z^{N} are the N^{15}-atomic fractions of ammonia $\mathrm{N^{15}H_3/(N^{14}H_3+N^{15}H_3)}$ and nitrogen $\mathrm{(N^{14}N^{15}+2N^{15}N^{15})/2(N^{14}N^{14}+N^{14}N^{15}+N^{15}N^{15})}$ respectively. Combining Eqs. (5.a) and (6.a) we have

$$\frac{V_+}{V_-}=\frac{a\dfrac{dZ^{\mathrm{A}}}{dt}\Big/2(Z^{\mathrm{N}}-Z^{\mathrm{A}})}{\left\{a\dfrac{dZ^{\mathrm{A}}}{dt}\Big/2(Z^{\mathrm{N}}-Z^{\mathrm{A}})\right\}-\dfrac{1}{2}\dfrac{da}{dt}} \tag{7. a}$$

$$=\frac{1}{1-(Z^{\mathrm{N}}-Z^{\mathrm{A}})d\ln P_{\mathrm{A}}/dZ^{\mathrm{A}}}\,, \tag{7. b}$$

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

$$\nu_r=\frac{RT\ln\left(\dfrac{P_{\mathrm{H}}^3P_{\mathrm{N}}}{P_{\mathrm{A}}^2}K_{\mathrm{S}}\right)}{RT\ln[1/\{1-(Z^{\mathrm{N}}-Z^{\mathrm{A}})d\ln P_{\mathrm{A}}/dZ^{\mathrm{A}}\}]}\,, \tag{8}$$

which enables us to evaluate ν_r 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)

$$\frac{V_+}{V_-}=\frac{\left\{n\dfrac{dZ^{\mathrm{N}}}{dt}\Big/(Z^{\mathrm{A}}-Z^{\mathrm{N}})\right\}+\dfrac{1}{2}\dfrac{da}{dt}}{n\dfrac{dZ^{\mathrm{N}}}{dt}\Big/(Z^{\mathrm{A}}-Z^{\mathrm{N}})} \tag{9. a}$$

$$=1+\frac{P_{\mathrm{A}}}{2P_{\mathrm{N}}}(Z^{\mathrm{A}}-Z^{\mathrm{N}})\frac{d\ln P_{\mathrm{A}}}{dZ^{\mathrm{N}}}\,. \tag{9. b}$$

Thus we obtain another equation for evaluating ν_r, *i. e.*

$$\nu_r=\frac{RT\ln\left(\dfrac{P_{\mathrm{H}}^3P_{\mathrm{N}}}{P_{\mathrm{A}}^2}K_{\mathrm{S}}\right)}{RT\ln\left\{1+\dfrac{P_{\mathrm{A}}}{2P_{\mathrm{N}}}(Z^{\mathrm{A}}-Z^{\mathrm{N}})\dfrac{d\ln P_{\mathrm{A}}}{dZ^{\mathrm{N}}}\right\}}\,. \tag{10}$$

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

$$Z^{\mathrm{A}}a+2Z^{\mathrm{N}}n=Z_t(a+2n) \tag{11. a}$$

or in terms of pressures

$$Z^{\mathrm{A}}P_{\mathrm{A}}+2Z^{\mathrm{N}}P_{\mathrm{N}}=Z_t(P_{\mathrm{A}}+2P_{\mathrm{N}})\,, \tag{11. b}$$

where Z_t 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

$$\nu_r = \frac{RT\ln\left(\dfrac{P_{\mathrm{H}}^3 P_{\mathrm{N}}}{P_{\mathrm{A}}^2} K_{\mathrm{S}}\right)}{RT\ln\left[1\Big/\left\{1-\left(1+\dfrac{P_{\mathrm{A}}}{2P_{\mathrm{N}}}\right)(Z_i-Z^{\mathrm{A}})\dfrac{d\ln P_{\mathrm{A}}}{dZ^{\mathrm{A}}}\right\}\right]}. \tag{12}$$

This equation is useful in evaluating ν_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 $Z^{\mathrm{N(a)}}$ of adsorbed nitrogen N(a) is equal to Z^{A} or to Z^{N}. Two functions ϕ and ψ are introduced to decide which is the case in the system specified in section 1.1.

The ϕ is defined as

$$\phi \equiv \frac{(Z_1^{\mathrm{N}})^2}{Z_0^{\mathrm{N}}\cdot Z_2^{\mathrm{N}}}\Big/K_{\mathrm{N}}, \tag{13}$$

where Z_0^{N}, Z_1^{N} and Z_2^{N} are the mole fractions of $\mathrm{N}^{14}\mathrm{N}^{14}$, $\mathrm{N}^{14}\mathrm{N}^{15}$ and $\mathrm{N}^{15}\mathrm{N}^{15}$ in gaseous nitrogen respectively, and K_{N} is the equilibrium constant for nitrogen isotopes equilibration, $\mathrm{N}^{14}\mathrm{N}^{14}+\mathrm{N}^{15}\mathrm{N}^{15}=2\mathrm{N}^{14}\mathrm{N}^{15}$. At the beginning of the reaction, nitrogen is normal so that the value of ϕ is unity independent of which is rate-determining. If step (2.I) is in partial equilibrium, ϕ continues at unity throughout the reaction since in that case the numerator $(Z_1^{\mathrm{N}})^2/Z_0^{\mathrm{N}}\cdot Z_2^{\mathrm{N}}$ is always equal to K_{N}. If the set of steps (2.III) is alternatively in partial equilibrium, ϕ 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 ϕ is caused by more rapid formation of $\mathrm{N}^{15}\mathrm{N}^{15}$ than $\mathrm{N}^{14}\mathrm{N}^{15}$ in an early stage of the reaction where $Z^{\mathrm{N(a)}}$ is close to unity, and by the amount of $\mathrm{N}^{14}\mathrm{N}^{14}$ far exceeding the amounts of $\mathrm{N}^{15}\mathrm{N}^{15}$ and $\mathrm{N}^{14}\mathrm{N}^{15}$ throughout the reaction.

The rates of formation of $\mathrm{N}^{14}\mathrm{N}^{15}$ and $\mathrm{N}^{15}\mathrm{N}^{15}$, *i.e.* $d(Z_1^{\mathrm{N}}n)/dt$ and $d(Z_2^{\mathrm{N}}n)/dt$, are given with reference to step (2.I) as

$$Z_1^{\mathrm{N}}\frac{dn}{dt}+n\frac{dZ_1^{\mathrm{N}}}{dt} = 2Z^{\mathrm{N(a)}}(1-Z^{\mathrm{N(a)}})v_{-1}-Z_1^{\mathrm{N}}v_{+1} \tag{14. a}$$

and

$$Z_2^{\mathrm{N}}\frac{dn}{dt}+n\frac{dZ_2^{\mathrm{N}}}{dt} = (Z^{\mathrm{N(a)}})^2v_{-1}-Z_2^{\mathrm{N}}v_{+1} \tag{14. b}$$

respectively, where v_{+1} is the unidirectional forward rate of step (2.I) and v_{-1}

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 $Z^{N(a)}$ 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 $Z^{N(a)}$ to Z^A yields

$$\frac{dZ_2^N}{dZ_1^N}=\frac{Z^A}{2(1-Z^A)}. \tag{15}$$

The function ψ defined as

$$\psi\equiv\frac{dZ_2^N}{dZ_1^N}\bigg/\frac{Z^A}{2(1-Z^A)} \tag{16}$$

is consequently equal to unity when the set of steps (2.III) is in partial equilibrium. The value of ψ 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 $N^{14}N^{15}$ since the value of $Z^{N(a)}$ is close to zero.

TABLE 1. Theoretical values for ν_r, ϕ and ψ for the alternative rate-determining step.

Rate-determining step		(2.I)	one of (2.III)	Stage of reaction where applicable
Values for	ν_r	1	2	valid throughout the reaction
	ϕ	$\simeq 0$	1	valid except in initial and final stages
	ψ	1	$\simeq 0$	valid only in early stage of decomposition

Table 1 summarizes values for ν_r, ϕ and ψ 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 ν_r on the tacit assumption that none of the reaction mixture is withdrawn at any time during the reaction. The determination of partial equilibrium using ψ is also based on this assumption. It is now proven that the proposed determinations of ν_r 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 $d\ln P_A/dZ^A$ with respect to time,

$$\frac{d\ln P_A}{dZ^A}=\frac{dP_A/dt}{P_A\,dZ^A/dt}. \tag{17}$$

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

$$V = \frac{V_r}{2RT}\,\frac{dP_A}{dt}\,, \tag{18}$$

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

$$V_+ = \frac{P_A V_r}{2(Z^N - Z^A)RT}\,\frac{dZ^A}{dt}\,. \tag{19}$$

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 ν_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 ϕ and ψ either. In the case of ϕ, this is evident from Eq. (13) without demonstration. In the case of ψ, this can be proven by rewriting the term dZ_2^N/dZ_1^N of Eq. (16) as $(dZ_2^N/dt)/(dZ_1^N/dt)$ and applying an argument similar to that made for ν_r.

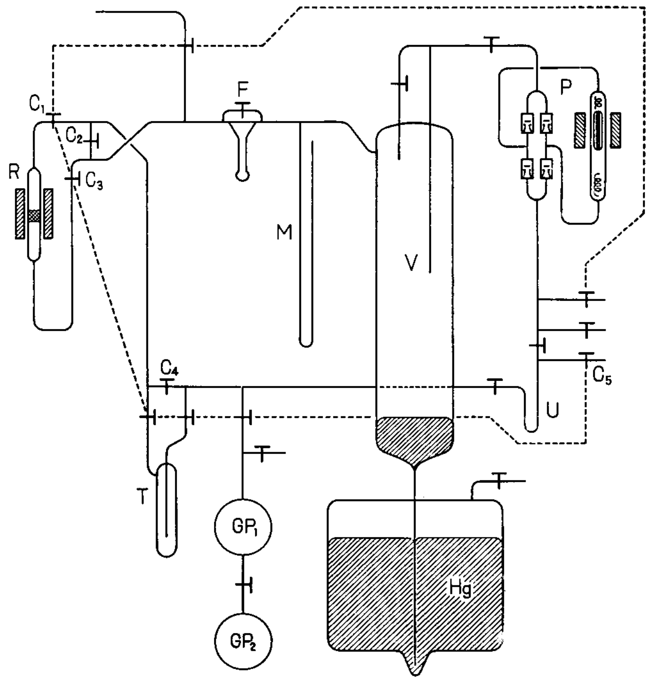

Fig. 1. Schematic diagram of the circulating system.
The broken lines enclose the circulating system, S_C. The circulating system, S_C, plus the reaction vessel, R, comprise the reaction system, S_R.

2. Experimental

2.1. Apparatus.

Fig. 1 is a schematic diagram of the circulating system used to measure ν_r, ϕ and ψ. 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_4 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 S_C, and the system "S_C+R" as reaction system S_R. When the mercury level in the cylinder was set to the lowest marker, the volume of the circulating system S_C was 2123 cc. The apparent volume*) 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.

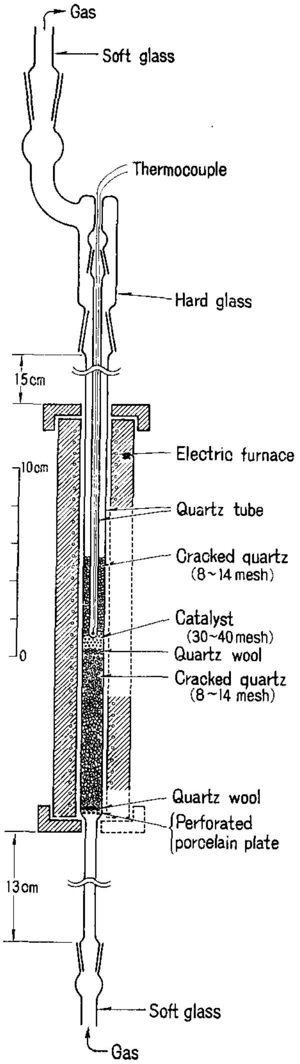

Fig. 2. Detailed illustration of the reaction vessel R.

The circulating system was attached to a $N^{15}H_3$-dosing device, an analyzing system, *etc.* respectively through a stopcock. Fig. 3 illustrates the $N^{15}H_3$-dosing device which has a gas burette B_1 and a $N^{15}H_3$ reservoir. The gas burette could be separated into two parts, one of them having a manometer, by closing stopcock C_6. 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_6 was closed or open. Fig. 4 illustrates the analyzing system with gas pipettes GP_1 and GP_2, two traps

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*) 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*.

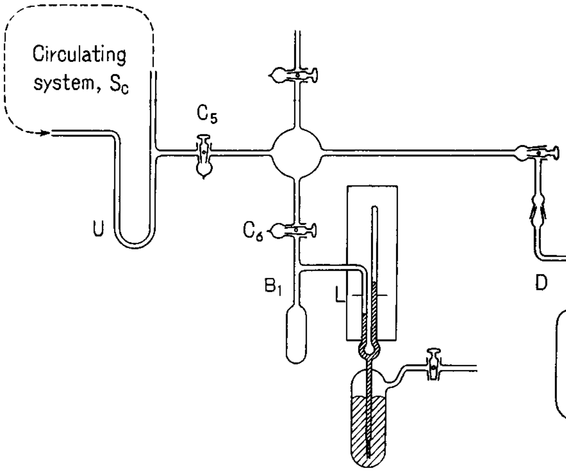

Fig. 3. $N^{15}H_3$-dosing device.

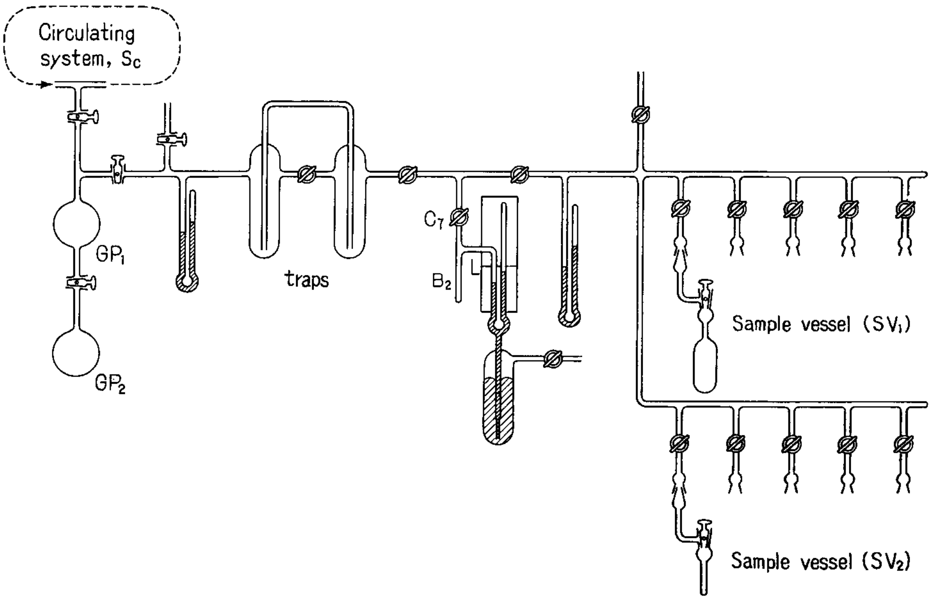

Fig. 4. Analyzing system.

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 $N^{15}H_3$-dosing device and had a volume of 2.71 or 8.73 cc.

2.2. Materials. The singly-promoted iron catalyst used to determine ν_r, ϕ and ψ 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% Al_2O_3) as used by BOKHOVEN and his coworkers[3)]. 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 furhter consumption. From the amount of hydrogen consumed, it was calculated that the catalyst was reduced completely (100%) on a basis of 99% Fe_3O_4 and 1% unreducible promotor[3)], 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 ν_r, ϕ and ψ. The 3:1 hydrogen-nitrogen mixture formed was passed through two liquid nitrogen traps in series to remove the undecomposed ammonia.

The N^{15}-enriched ammonia was prepared by gently heating a powdered mixture of N^{15}-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 N^{15}-enriched ammonium sulfate was purchased from Rikagaku Kenkyusho (The Institute of Physical and Chemical Research), Tokyo. It was stated to be 99 N^{15}-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. N^{15}-enriched ammonia was first admitted to gas burette B_1 of the $N^{15}H_3$-dosing device where its pressure was determined, and then transferred to U by means of liquid nitrogen.[**)] Stopcock C_5 was closed and U was warmed to a room temperature, and the evaporated N^{15}-enriched ammonia and the 3:1 hydrogen-nitrogen mixture was circulated through by-pass stopcocks C_2 and C_4. The pressure of the resulting mixture ($H_2+N_2+N^{15}H_3$), 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 GP_1 or GP_1+GP_2 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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*) Cf. footnote on page 129.

**) Gas burette B_1 could measure pressures of less than 150 mmHg. When more ammonia was needed this procedure was repeated.

section 2.4. The gas admitted into the gas pipette was further analyzed in a mass spectrometer for $N^{15}H_3$, $N^{14}N^{15}$ and $N^{15}N^{15}$ in order to determine Z^A, Z_1^N and Z_2^N. 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 GP_1 or GP_1+GP_2 and analyzed to determine P_A, Z^A, Z_1^N and Z_2^N. 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 ±3 mmHg and ±1°C. The room temperature was set at 23±1°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 S_C-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°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 2. Reaction conditions.

Run	Catalyst	Decompn. or synthesis	Reaction temp. (°C)	Pressure (mmHg)			Reaction time (hrs)	Remarks
				total	ammonia			
					(initial)	(final)		
1	1.51 g of singly-promoted Fe	syn	300	420	1.6	1.8	73	unsuccessful
2		〃	340	550	1.6	3.6	92	
3		〃	〃	〃	1.7	3.8	124	
4		dec	〃	〃	8.0	3.8	128	
5		syn	305	〃	3.4	6.5	302	
6		dec	〃	〃	11.4	7.4	528	
7		syn	340	〃	1.9	3.7	69	
8	none	(〃)	〃	〃	1.8	1.9	26	blank run without catalyst
9	〃	(dec)	〃	〃	7.0	7.0	30	
10	〃	(syn)	〃	〃	1.7	1.7	7	

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*) 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 C_1 and C_3 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 3×10^{-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 GP_1 or GP_1+GP_2 was analyzed for total ammonia, $N^{15}H_3$, $N^{14}N^{15}$ and $N^{15}N^{15}$ 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 SV_1 and the remainder was slowly pumped out. The ammonia frozen out in the traps was evaporated, transferred to gas burette B_2, and its pressure was read. The partial pressure $P_{A,obs.}$ of ammonia in circulating system S_C or the partial pressure P_A of ammonia in reaction system S_R was determined from this pressure read and the volume ratio of GP_1 or GP_1+GP_2 to B_2 using BOYLE's law. Before the reaction was begun, the total pressure of the gas mixture in S_C was somewhat higher than 550 mmHg as has been described in section 2.3. The values for P_A at $t=0$, *i.e.* at the beginning of the reaction, was therefore taken as $550\,P_{A,obs.}/P_{T(0)}$ (mmHg), where the average of several measurements was used for $P_{A,obs.}$, and $P_{T(0)}$ was the total pressure of the gas mixture in S_C at $t=0$. The partial pressures P_H and P_N were taken as $P_H=\frac{3}{4}(550-P_A)$ and $P_N=\frac{1}{4}(550-P_A)$ (mmHg) respectively.

The ammonia in gas burette B_2 was then transferred to one of sample vessels SV_2 for mass spectrometric analysis to determine Z^A. The analysis was kindly carried out by Prof. K. MIYAHARA with a mass spectrometer, which he constructed,[4]*) 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 $N^{15}H_3$ to $N^{14}H_3$ after the contribution to *m/e* 18 by the $N^{14}H_4^+$ ion and to *m/e* 17 by the $N^{15}H_2^+$ ion were corrected.

The mixture of hydrogen and nitrogen admitted to SV_1 was analyzed for $N^{14}N^{15}$ and $N^{15}N^{15}$ 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 $N^{14}N^{14}H^+$ through a mechanism, *e.g.* $N_2^+ + H_2 \longrightarrow N_2H^+ + H$. It follows from this mechanism that the contribution to *m/e* 29 by the $N^{14}N^{14}H^+$ ion is proportional to P^2. On the other hand, the contribution to *m/e* 29 by the $(N^{14}N^{15})^+$ ion as well as the contribution to *m/e* 28 by $(N^{14}N^{14})^+$ ion appears proportional to P. Then, the ratio *m/e* 29 to 28 increases linearly with P as was actually observed, and the ratio $N^{14}N^{15}$ to $N^{14}N^{14}$ 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 $N^{14}N^{15}$ to $N^{15}N^{15}$ 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 $N^{14}N^{15}$ to $N^{14}N^{14}$ ratio was 0.00721 as compared with the theoretical value 0.00729, which was derived from the natural abundance

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*) This mass spectrometer was designated in reference (4) as "mass spectrometer II".

0.365% of N^{15} and the equilibrium constant 4 for the nitrogen isotopes equilibration, $N^{14}N^{14} + N^{15}N^{15} = 2N^{14}N^{15}$. This close agreement gives considerable confidence to the above procedure for determining the $N^{14}N^{15}$ to $N^{14}N^{14}$ ratio. On the other hand, the m/e 30 to 28 ratios measured at various P were averaged, and the mean value was taken as the ratio of $N^{15}N^{15}$ to $N^{14}N^{14}$.

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 R was opened, *i. e.* at reaction time $t=0$. These samples are designated as O_a, O_b, O_c, *etc.*, in order of sampling, and generically as "O". In Table 4, the values for $P_{A,obs.}$ are listed for each of these samples O.

As may be seen from Tables 2 and 3, in each run, P_A was negligibly small in comparison with the total pressure, 550 mmHg. In consequence, the volume V_i of reaction system 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 V_i decreased stepwise every time a sample was taken, as is shown in Tables 3.

TABLE 3a. Run 3. Ammonia synthesis and N^{15}-exchange between ammonia and nitrogen.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A
0	0	2258	1.96	0.961
1	0.3	2072	1.73	0.816
2	5.0	1864	2.26	0.723
3	13.8	1766	2.68	0.567
4	24.8	1669	3.00	0.461
5	37.8	1578	3.32	0.360
6	57.8	1486	3.59	0.266
7	77.8	1386	3.67	0.194
8	101.8	1288	3.78	0.126
9	123.8		3.80	0.129

t, reaction time; V_i, volume of reaction system S_R (reaction vessel R + space enclosed by broken lines in Fig. 1) during the interval between two successive samplings; P_A, partial pressure of ammonia in reaction system S_R; Z^A, N^{15}-atomic fraction of ammonia.

TABLE 3 b. Run 4. Ammonia decomposition and N^{15}-exchange between ammonia and nitrogen.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A	Z_1^N	Z_2^N	Z^N
0	0	2257	7.97	0.951			
1	0.5	2160	7.45	0.905			
2	3.0	2071	7.19	0.890	0.0078	0.0010	0.0049
3	10.0	1975	6.23	0.836	0.0092	0.0060	0.0106
4	19.0	1878	5.34	0.745			
5	26.0	1792	4.72	0.658			
6	35.0	1698	4.25	0.554	0.0161	0.0145	0.0226
7	47.0	1599	4.15	0.416			
8	59.0	1507	4.04	0.300	0.0230	0.0167	0.0282
9	80.0	1410	3.97	0.166	0.0274	0.0164	0.0301
10	105.0	1318	3.96	0.084	0.0305	0.0176	0.0329
11	128.0		3.76	0.033	0.0322	0.0171	0.0332

Z_1^N, mole fraction of $N^{14}N^{15}$ in nitrogen; Z_2^N, mole fraction of $N^{15}N^{15}$ in nitrogen; Z^N, N^{15}-atomic fraction of nitrogen.

TABLE 3 c. Run 5. Ammonia synthesis and N^{15}-exchange between ammonia and nitrogen.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A	Z_1^N	Z_2^N	Z^N
0	0	2242	3.71	0.930			
1	0.5	2144	3.39	0.851			
2	5.0	2052	3.46	0.822	0.0074	0.0002	0.0039
3	21.0	1952	3.77	0.755			
4	36.0	1862	3.83	0.709	0.0077	0.0007	0.0046
5	57.0	1761	4.57	0.625	0.0088	0.0013	0.0057
6	82.0	1662	4.78	0.580			
7	115.0	1563	5.22	0.507	0.0095	0.0017	0.0065
8	160.0	1474	5.69	0.441			
9	203.0	1370	5.96	0.358			
10	251.0	1273	6.29	0.323	0.0135	0.0031	0.0099
11	302.1		6.53	0.273			

TABLE 3d. Run 6. Ammonia decomposition and N^{15}-exchange between ammonia and nitrogen.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A	Z_1^N	Z_2^N	Z^N
0	0	2258	11.89	0.976			
1	0.5	2165	11.44	0.944			
2	5.0	2079	11.39	0.933			
3	22.0	1984	11.14	0.936			
4	48.0	1885	10.77	0.905	0.0082	0.0029	0.0070
5	78.0	1792	10.33	0.879			
6	116.0	1697	9.93	0.847	0.0093	0.0069	0.0116
7	163.0	1607	9.47	0.778	0.0103	0.0107	0.0159
8	211.0	1508	8.98	0.738	0.0120	0.0132	0.0192
9	267.0	1411	8.59	0.672	0.0145	0.0151	0.0224
10	338.0	1320	8.21	0.587	0.0166	0.0182	0.0265
11	428.0	1239	7.73	0.496	0.0204	0.0205	0.0308
12	528.0		7.44	0.405			

TABLE 3e. Run 7. Ammonia synthesis and N^{15}-exchange between ammonia and nitrogen.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A
0	0	2099	2.11	0.824
1	0.5	1999	1.92	0.783
2	3.0	1908	2.27	0.631
3	6.8	1803	2.86	0.474
4	12.0	1706	3.29	0.362
5	17.0	1611	3.42	
6	24.0	1515	3.62	0.211
7	32.0	1418	3.71	0.134
8	41.0	1322	3.82	
9	53.0	1236	3.71	
10	69.0		3.71	

TABLE 3f. Run 8. Blank run without catalyst.

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A
0	0	2206	1.95	0.904
1	0.5	2115	1.83	0.905
2	4.0	2020	1.72	0.904
3	8.0	1920	1.83	0.897
4	15.0	1832	1.87	0.904
5	22.0	1739	1.88	0.920
6	26.0		1.87	0.902

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

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A
0	0	2252	7.10	0.937
1	0.5	2161	7.04	0.944
2	3.0	2065	6.93	0.951
3	6.0	1963	7.03	0.951
4	11.0	1869	6.98	
5	19.0	1775	6.99	0.949
6	30.0		6.95	0.953

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

Sample	t (hr.)	V_i (cc)	P_A (mmHg)	Z^A
0	0	2197	1.68	0.936
1	0.5	1995	1.67	0.938
2	3.0	1791	1.74	0.935
3	7.0		1.73	0.938

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

Run	Sample	Time (hr.)	V_i' (cc)	P_T (mmHg)	$P_{A,calc.}$ (mmHg)	$P_{A,obs.}$ (mmHg)	P_{AG} (mmHg)
3	O_a	1.0	2123	615	2.54	2.20	0.34
	O_b	8.1		〃	〃	2.18	0.36
4	O_a	1.0	2123	621	9.31	9.00	0.31
	O_b	5.0		〃	〃	8.99	0.32
5	O_a	1.0	2123	609	4.42	4.08	0.34
	O_b	4.0		〃	〃	4.13	0.29
6	O_a	1.0	2123	614	13.63	13.26	0.37
	O_b	4.0		〃	〃	13.27	0.36
7	O_a	1.0	2123	607	2.57	2.31	0.26
	O_b	5.3	2028	〃	〃	2.36	0.21
	O_c	24.7		〃	〃	2.33	0.24
8	O_a	0.5	2123	597	2.40	2.09	0.31
	O_b	3.0		〃	〃	2.14	0.26
9	O_a	0.5	2123	652	8.80	8.43	0.37
	O_b	3.0	2040	〃	〃	8.46	0.34
	O_c	20.0		〃	〃	8.36	0.44
10	O_a	3.0	2123	696	2.42	2.14	0.28
	O_b	24.1	?	〃	〃	2.12	0.30
	O_c	115.3	1829	〃	〃	2.08	0.34
	O_d	167.2		〃	〃	2.12	0.30
						Mean	0.32

Sample has been defined on page 131. Time is the time allowed for the mixture of H_2, N_2 and $N^{15}H_3$ 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_i' 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.* $P_{AG} \equiv P_{A,calc.} - P_{A,obs.}$.

TABLE 5. Mass spectrometric analysis of a series of ammonia samples in run 6 to determine memory effect.

Sample	Z^A		
O_a	0.980		0.975
O_b	(0.938)	0.972	
1	0.942	0.957	0.932
2	0.925	0.948	0.932
3	0.928	0.939	0.940
4	0.898	0.899	0.917
5	0.883	0.888	0.867
6	0.847		
7	0.778		
8	0.738		
9	0.672		
10	0.587		
11	0.496		
12	0.405		

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 comparion 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, $(P_A)_e$, 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 $(P_{\mathrm{A}})_e$ values that the equilibrium constant K_{S} of ammonia synthesis (1) is 1.54×10^{-9} and 5.34×10^{-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,[5] $\log K_{\mathrm{S}}=2\times\{2.098.2/T-2.509\log T-1.006\times10^{-4}\,T+1.860\times10^{-7}\,T^2+2.10\}$, *i.e.* 2.05×10^{-9} mmHg^{-2} at 340°C, 6.99×10^{-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 $(P_{\mathrm{A}})_e$ are 4.38 mmHg

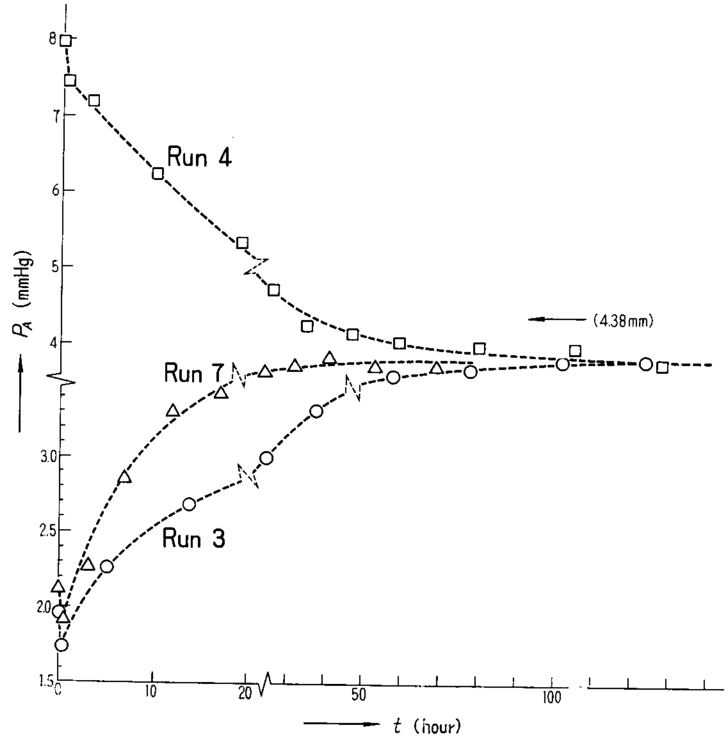

Fig. 5 a. The pressure of ammonia plotted against time at 340°C. Arrow shows the pressure of ammonia in equilibrium as derived by HABER's equlibrium constant.

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*) In each run, the derivative dP_{A}/dt was discontinuous each time a sample was taken because of a stepped descrease 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 $(P_{\mathrm{A}})_e$. The discontinuity will be discussed in more detail in the future.

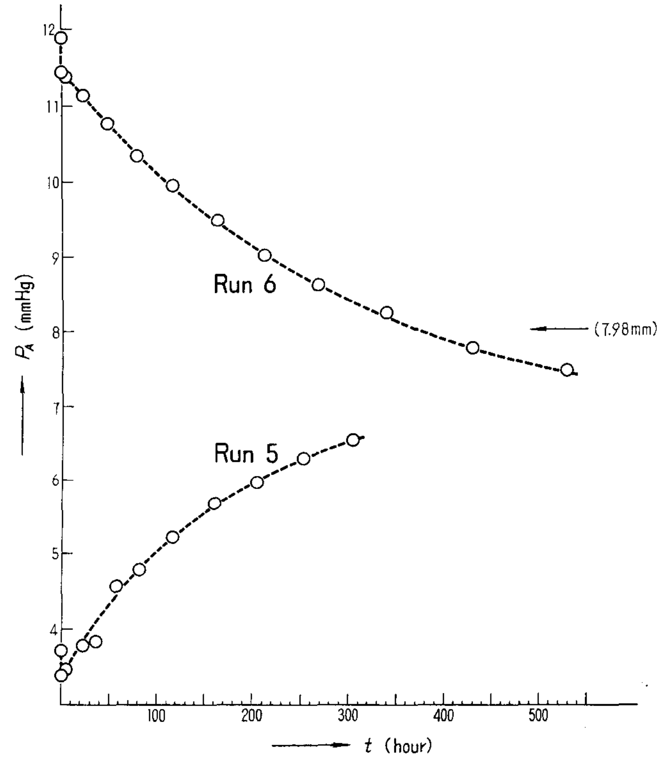

Fig. 5 b. The pressure of ammonia plotted against time at 305°C. Arrow shows the pressure of ammonia in equilibrium as derived by HABER's equilibrium constant.

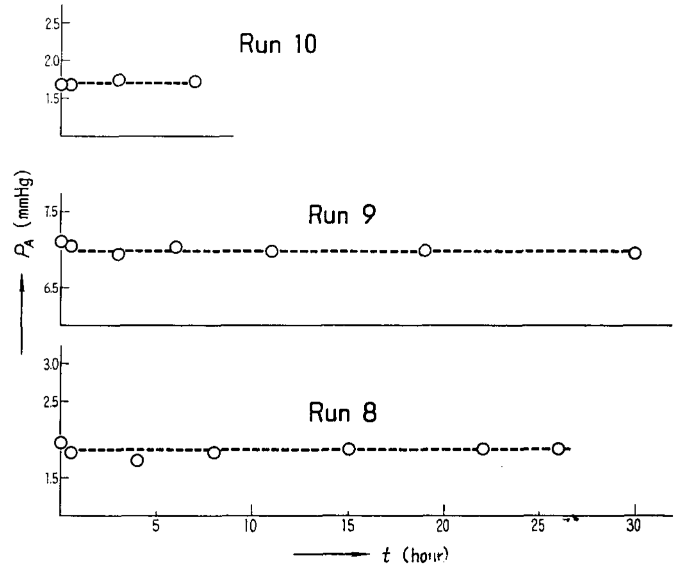

Fig. 5 c. The pressure of ammonia plotted against time in blank runs (340°C).

at 340°C and 7.98 mmHg at 305°C under the conditions of the present work. ENOMOTO and HORIUTI[6] 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^{15}-enriched ammonia was admitted from gas burette B_1 to circulating system S_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_C from the volumes of B_1 and S_C and the pressure determined in B_1. The values thus calculated, $P_{A,calc.}$, are compared with $P_{A,obs.}$ in Table 4. The difference, $P_{A,calc.} - P_{A,obs.}$, 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_1 connected with gas reservoir D was filled with nitrogen and the pressure was read with the manometer of B_1. The nitrogen was then allowed to expand into both circulating system S_C and Mcleod gauge E temporarily attached to S_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_C and communicating part.

Part of the apparatus containing N_2 or $N^{15}H_3$	N_2 admitted		$N^{15}H_3$ admitted		$P_{N_2} \times \frac{49.89}{48.87} - P_{N^{15}H_3}$
	time (min)	P_{N_2} (mmHg)	time (min)	$P_{N^{15}H_3}$ (mmHg)	
B_1+D		48.87		49.89	0.00
B_1+D+S_C+E	12	2.50	5	2.28	0.27
"	30	2.50	20	2.27	0.28
"			960	2.20	0.35
"			2760	2.19	0.36
"			3960	2.18	0.37

D: gas reservoir attached to gas burette B_1.
E: Mcleod gauge temporarily attached to circulating system S_C.
Time: time elapsed following expansion of N_2 or $N^{15}H_3$ into space B_1+D+S_C+E.

N^{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 $(49.89\,P_{N_2}/48.87)-P_{N^{15}H_3}$ is the difference between the pressures of nitrogen and N^{15}-enriched ammonia which would have resulted had the same amount of nitrogen and N^{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, ($P_{A,\text{calc.}}-P_{A,\text{obs.}}$, 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_{AG}, *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 μmoles or 2.2×10^{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 Å^2,[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,[8] the adsorption of ammonia on glass wool extended to 12 molecular layers at 0°C and one atmosphere. EVANS and GEORGE[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[10] found $1\sim6\times10^{17}$ molecules of ammonia to be adsorbed on the walls of McLeod gauge and connecting tubing at 21°C over a pressure range of $10^{-3}\sim10^{-1}$ mmHg.

As is evident in Figs. 5 a and 5 b, 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

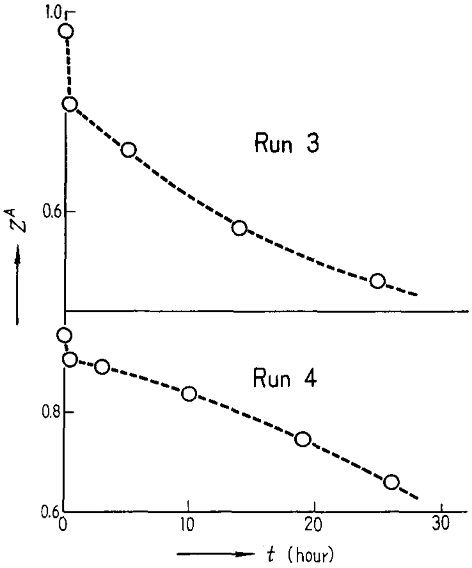

Fig. 6. Typical rapid drop in Z^A in the initial stage of the reaction.

$$a_C = P_{AC} V_i / RT, \tag{20}$$

where P_{AC} is the difference in P_A value between samples 0 and 1. Putting T as 296°K and V_i 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.

TABLE 7. Adsorbed ammonia and residual nitrogen on the catalyst.

Run	Syn. or decompn.	Temp. (°C)	P_A of Sample 1 (mmHg)	a_C (μmole)	n_R (μmole)
3	Syn.	340	1.73	28	51
4	decompn.	"	7.45	63	53
5	syn.	305	3.39	39	47
6	decompn.	"	11.44	55	51
7	syn.	340	1.92	22	—
				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^{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^{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^{15}-atoms between the residual nitrogen and the N^{15}-enriched ammonia. Assuming that when sample 1 was taken, N^{15}-atoms were evenly distributed among the residual nitrogen, gaseous ammonia and adsorbed ammonia, and neglecting the transfer of N^{15}-atoms to gaseous nitrogen, we have

$$Z^A_{(0)}(a_{(1)}+a_G+a_C)+Z^{N(R)}n_R = Z^A_{(1)}(a_{(1)}+a_G+a_C+n_R)\,, \tag{21}$$

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)

$$n_R = (a_{(1)}+a_G+a_C)\frac{Z^A_{(0)}-Z^A_{(1)}}{Z^A_{(1)}-Z^{N(R)}}\,. \tag{22}$$

The $Z^{N(R)}$ value not actually measured may be identified with the average value 0.03 of Z_i, 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^{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_i from Eq. (11.b) the N^{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^{15}, as mass spectrometric determination of Z^N was unsuccessful for these samples. As is shown in Table 8, the Z_i value thus calculated appears to decrease rapidly in the early stage of the reaction and then slowly increase.

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*) $a_{(1)}=P_A V_{0\sim 1}/RT$, where $V_{0\sim 1}$ is the value of V_i in liter during the interval between samples 0 and 1.

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 N^{15}-atoms beween the ammonia and the residual nitrogen as was discussed in the preceeding section. The later slow increase in Z_i is probably attributable to the gradual transfer of N^{15}-atoms from the adsorbed ammonia on the catalyst and glass walls to the gaseous ammonia and gaseous nitrogen.

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

$$Z'_i = \frac{Z^{A}_{(0)}(a_{(0)}+a_{G})+Z^{N(R)}n_{R}+2Z^{N}_{(0)}n_{(0)}}{a_{(0)}+a_{G}+n_{R}+2n_{(0)}} \qquad \text{for sample 0} \qquad (23.\text{a})$$

and

$$= \frac{Z^{A}_{(i)}(a_{(i)}+a_{G}+a_{C}+n_{R})+2Z^{N}_{(i)}n_{(i)}}{a_{(i)}+a_{G}+a_{C}+n_{R}+2n_{(i)}} \qquad \text{for sample } i\ (i \geqq 1), \qquad (23.\text{b})$$

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'_i from

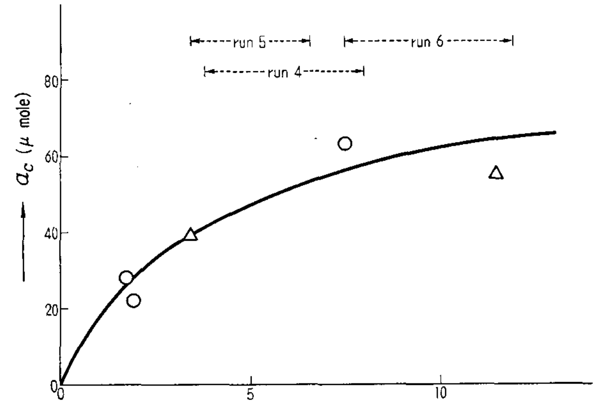

Fig. 7. The amount of ammonia adsorbed on the catalyst plotted against pressure of ammonia.
○ : 340°C, △ : 305°C, |←······→| : Range of P_A in each run.

Eqs. (23.b), a_G and n_R were taken as 37 and 51 μmoles 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 μmoles for runs 4, 5 and 6, respectively. The values of $a_{(0)}$ and $a_{(i)}$ 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'.

Run	4		5		6	
Z_i or Z_i' / Sample	Z_i	Z_i'	Z_i	Z_i'	Z_i	Z_i'
0	0.0307	0.0317	0.0161	0.0170	0.0446	0.0457
1						
2	0.0277	0.0313	0.0141	0.0174		
3	0.0291	0.0326				
4			0.0144	0.0174	0.0440	0.0458
5			0.0159	0.0188		
6	0.0307	0.0334			0.0412	0.0456
7			0.0159	0.0185	0.0417	0.0459
8	0.0322	0.0337			0.0423	0.0465
9	0.0321	0.0329			0.0424	0.0465
10	0.0336	0.0340	0.0170	0.0190	0.0430	0.0468
11	0.0332	0.0332			0.0437	0.0471

3. 5. ν_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 ν_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 ν_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

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*) $a_{(i)} = P_A V_{i-1\sim i}/RT$, where $V_{i-1\sim i}$ is the value of V_i in liter during the interval between samples $i-1$ and i. When $i=0$, however, $a_{(0)} = P_A(V_{0\sim 1}+0.095)/RT$, where 0.095 is the volume in liter of gas pipette GP_1.

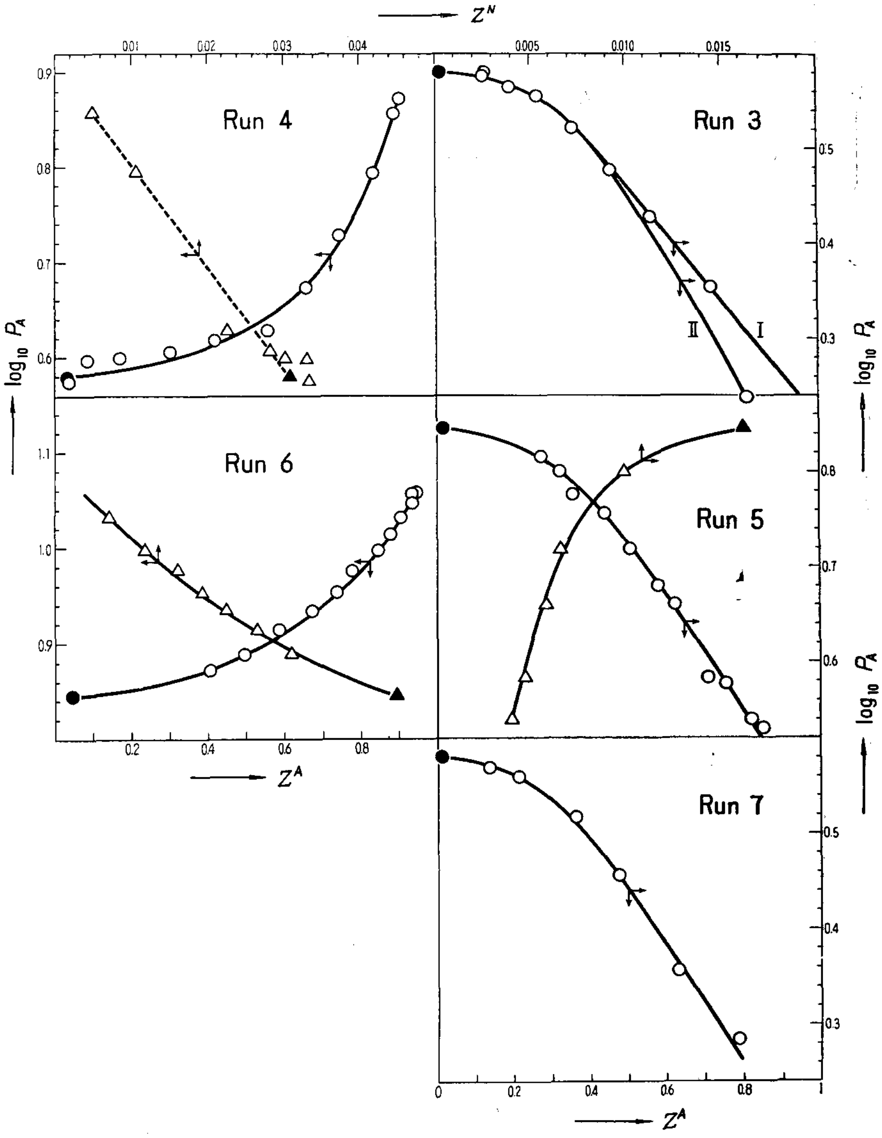

Fig. 8. Logarithm of P_A (pressure of ammonia) against Z^A (N^{15}-atomic fraction of ammonia) or Z^N (N^{15}-atomic fraction of nitrogen).

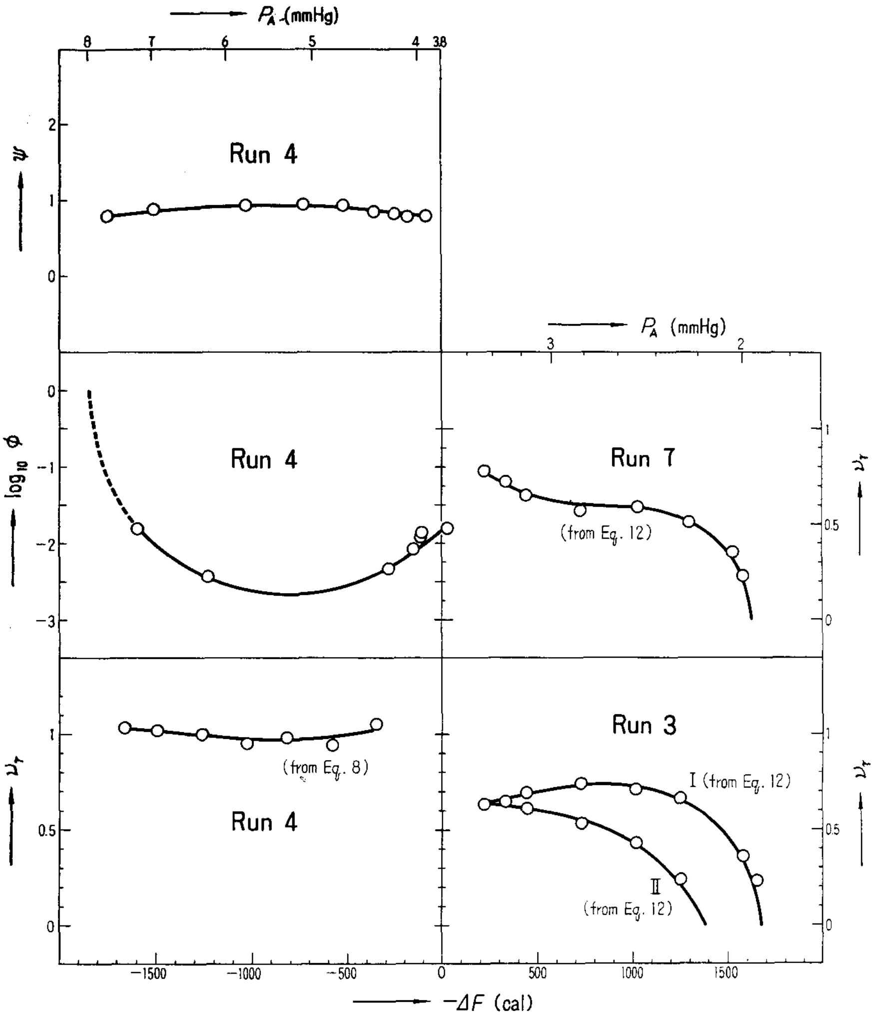

Fig. 9a. Observed values for ν_r, ϕ and ψ at 340°C as a function of chemical affinity.

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 ν_r.

In decomposition runs 4 and 6, the ν_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.I) is rate-determining. In run 6, this is further confirmed by calculating ν_r from equation (10). The values obtained from the latter equation are also near unity although the devia-

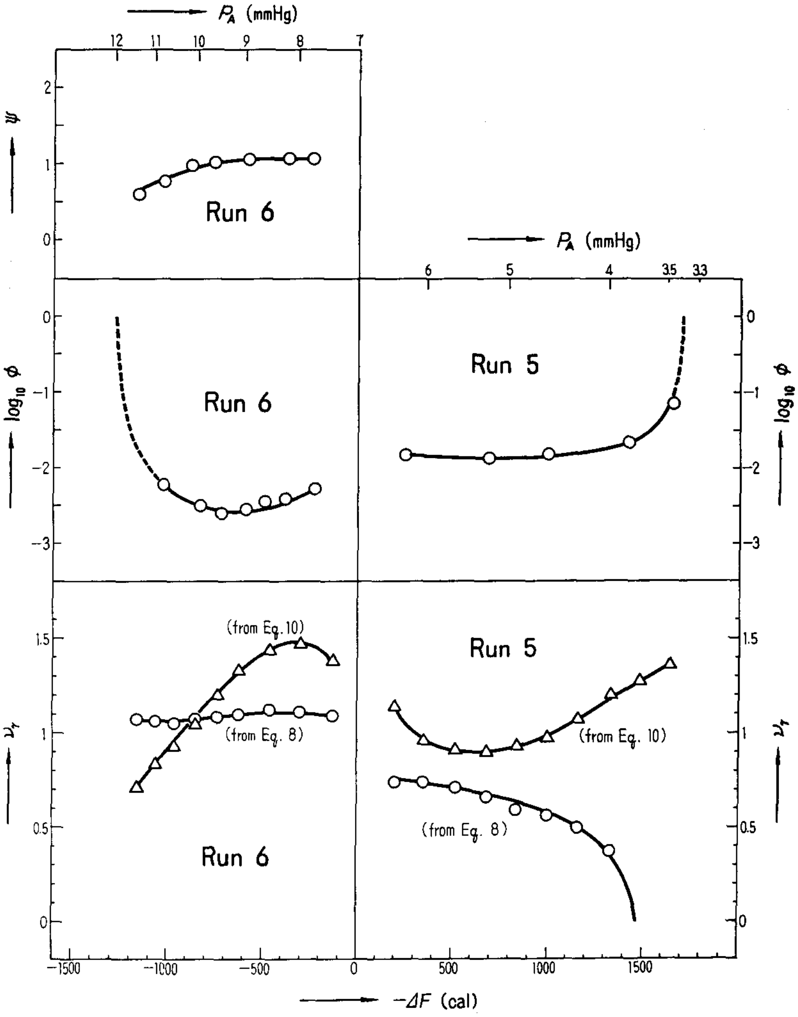

Fig. 9 b. Observed values for ν_r, ϕ and ψ at 305°C as a function of chemical affinity.

tions from unity are greater than those obtained from Eq. (8).

In synthesis run 5, the ν_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.I) is rate-determining. In contrast, the ν_r values calculated from Eq. (8) are a little lower than unity (~ 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 $\ln[1/\{1-(Z^N-Z^A)d\ln P_A/dZ^A\}]$ is negative. The same tendency is seen with ν_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 ν_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 ν_r may be disclosed especially if Eq. (8) or (12) is used in the synthesis run, and that by correcting for the adsorption, ν_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. ϕ and φ. The ϕ 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 ϕ is practically zero over most region of chemical affinity studied, providing additional evidence that step (2.I) is rate-determining.

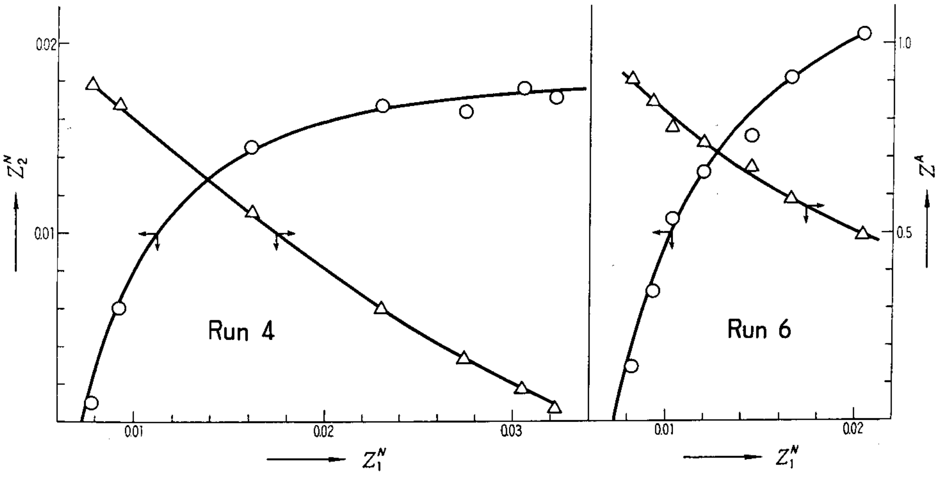

Fig. 10. Z_2^N and Z^A plotted against Z_1^N for runs 4 and 6.

Fig. 10 shows the Z_1^N *vs.* Z_2^N and Z_1^N *vs.* Z^A curves for runs 4 and 6. At various Z_1^N values, the Z^A value and tangent dZ_2^N/dZ_1^N were read to calculate φ using Eq. (16). The values calculated are plotted against chemical affinity in Figs. 9a and 9b. It may be seen that φ is near unity over the entire region of chemical affinity studied, further verifying that step (2.I) is rate-determining.

3.7. Conclusion. From the values for ν_r, ϕ and φ observed, it may be unambiguously concluded that step (2.I), *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 ν_r 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.

Acknowledgment

The author is greatly indebted to the former director of the Research Institute for Catalysis, Hokkaido University, Dr. J. HORIUTI, Professor emeritus, who suggested an idea of measuring ν_r in a region remote from equilibrium, corrected the manuscript and whose discussion and comments were invaluable in the present work. The author wishes to express his thanks to Prof. K. MIYAHARA, Hokkaido Univ., for the mass spectrometric analyses of ammonia and discussion of the results, and to Dr. N. MORITO, Dr. J. OKAMOTO and Dr. H. TSUYAMA, Hitachi Co. Ltd., for the mass spectrometric analyses of nirtogen. Dr. C. BOKHOVEN, the Netherlands, provided the singly-promoted iron catalyst, and Mrs. N. C. KNIGHT, National Center for Atmospheric Research, Colorado, U. S. A., corrected English. The author is also grateful for Mr. KODERA's friendly concern and valuable discussions throughout the course of this work.

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