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THE RATE-DETERMINING STEP OF AMMONIA SYNTHESIS AND DECOMPOSITION

Part 3. Study of the Reaction over a Singly-Promoted Iron Catalyst at 340-390°C[*]

By

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Abstract

In previous experiments in this series, nitrogen-15 was used as a tracer over a singly-promoted iron catalyst to determine ν_r as well as to directly locate the quasi-equilibrated steps at 305 and 340°C. In the experiments reported here these tracer studies have been extended to higher temperatures up to 390°C using the same catalyst. Most of the observed values for ν_r were close to one, and the chemisorbed nitrogen was found to be in quasi-equilibrium with the gas phase ammonia, as previously observed in the lower temperature region. From these results it is concluded that in a temperature range of 305 to 390°C, nitrogen chemisorption and desorption are rate-determining for ammonia synthesis and decomposition respectively.

Introduction

Part 1[1] and 2[2] of this series presented a new kinetic method of determining ν_r (the stoichiometric number of the rate-determining step) as well as locating quasi-equilibrated steps for ammonia synthesis and decomposition. This method was applied to reactions over a singly-promoted iron catalyst at 305 and 340°C. Over a wide range of ammonia pressures, the observed ν_r values were close to one, and chemisorbed nitrogen or other nitrogen-containing species was found to be in quasi-equilibrium with gas phase ammonia but not with gas phase nitrogen. These results lend support to the generally accepted view that nitrogen chemisorption and desorption are

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rate-determining for ammonia synthesis and decomposition respectively.

In advance of the work mentioned above, ENOMOTO *et al.*[3,4] and BOKHOVEN *et al.*[5] also measured ν_r for these reaction. The values observed by ENOMOTO *et al.* were close to two in conflict with the results of TANAKA. Although BOKHOVEN *et al.* reported a ν_r value of one in support of the TANAKA's results the rigidity of their analysis has been criticized later[6-8]. A ν_r value of two suggests that it is not the nitrogen chemisorption but the hydrogenation of chemisorbed nitrogen that is rate-determining. ENOMOTO *et al.* used higher reaction temperatures than those used by TANAKA; 430 and 450°C *versus* 305 and 340°C. These differences in reaction temperature may be significant since there are some indications[9,10] that the rate-determining step may change from chemisorption to hydrogenation as the temperature is raised. Thus, the kinetic studies introduced in the previous work would be worth extending to the higher temperature range used by ENOMOTO to test for a possible switch in the rate-determining step. In the actual experiments, however, the temperature was limited to 390°C so that the equilibrium pressure of ammonia, around which ν_r being measured, would not be too low. At lower ammonia pressures of approximately 2 mmHg, it has been observed[1,2] that, the amount of ammonia adsorbed on the catalyst and on the apparatus walls was comparable to that of the gas phase ammonia, thus making an accurate evaluation of ν_r extremely difficult. Surprisingly, ENOMOTO and HORIUTI[3] did not observe any adsorption during their ν_r measurements despite conditions more favorable for the detection of ammonia adsorption, *i.e.*, much lower ammonia pressures and larger catalyst sizes than used by TANAKA[1].

1. Theoretical

Several expressions for ν_r have been given in a previous paper[2], and a new expression is added in this report. Some of the data of the present studies will be analyzed using the new expression, and some by those expressions previously given. For the derivation of the new expression it is necessary to briefly repeat some of the previous theoretical considerations[1,2].

1.1. Reaction System Under Consideration. The reaction system to be treated may be defined as a system in which a non-equilibrium mixture of hydrogen, nitrogen, and N^{15}-labeled ammonia is circulated over a synthetic ammonia catalyst. The production or consumption of ammonia as well as the transfer of N^{15}-atoms from ammonia to nitrogen are followed simultaneously. Some of the ammonia may be adsorbed on the catalyst, the

apparatus walls, or both, in rapid quasi-equilibrium*) with the gas phase ammonia. Expressions for evaluating ν_r are derived below either with or without a correction for this adsorption.

1.2. ν_r. In the presence of a single rate-determining step we have, for any chemical reaction, the general relation

$$\nu_r = \frac{-\varDelta G}{RT \ln (V_+/V_-)} \, , \qquad\qquad (1)$$

where $-\varDelta G$ is the chemical affinity associated with the overall reaction, R is the gas constant, T is the reaction temperature, and V_+ and V_- are the unidirectional forward and backward rates respectively. For ammonia synthesis,

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

the chemical affinity may be expressed in terms of the equilibrium constant K_S, and the pressures of hydrogen P_H, nitrogen P_N, and ammonia P_A as

$$-\varDelta G = RT \ln (P_H^3 P_N K_S/P_A^2). \qquad\qquad (3)$$

The net rate V may be written as

$$V = V_- - V_- = \frac{1}{2}\frac{d(a + a_{(a)})}{dt} = -\frac{dn}{dt}, \qquad\qquad (4)$$

where a, $a_{(a)}$, and n are the numbers of moles of gaseous ammonia, adsorbed ammonia, and gaseous nitrogen respectively, and t is the reaction time. If $a_{(a)}$ is constant over the P_A range under study, as in the case previouly reported[1], Eq. (4) reduces to

$$V = V_+ - V_- = \frac{1}{2}\frac{da}{dt} \qquad\qquad (5.\,a)$$

$$= -\frac{dn}{dt}. \qquad\qquad (5.\,b)$$

The rate of N^{15} transfer from ammonia to nitrogen may be expressed as

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

or

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

where Z^A and Z^N are the N^{15}-atomic fractions of ammonia, $N^{15}H_3/(N^{14}H_3 + N^{15}H_3)$, and of nitrogen, $(N^{14}N^{15} + 2N_2^{15})/2(N_2^{14} + N^{14}N^{15} + N_2^{15})$, respectively.

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*) This term is substituted for the term "partial equilibrium" previously used[1,2].

Solving Eqs. (5. a) and (6. a) for V_+/V_- and assuming ideal gas behavior for ammonia, we finally obtain, as an expression for ν_r,

$$\nu_r = \frac{\ln (P_H^3 P_N K_S/P_A^2)}{\ln\left[1\Big/\left\{1+(Z^A-Z^N)\Big(\frac{1}{P_A'}\Big)\Big(\frac{dP_A}{dZ^A}\Big)\right\}\right]},\qquad(7)$$

where

$$P_A' = P_A + (a_{(a)}RT/V_i),\qquad(8)$$

V_i representing the volume of the reaction system. With reference to Eq. (8), it may be seen that if the ammonia adsorption is neglected, Eq. (7) reduces to

$$\nu_r = \frac{\ln (P_H^3 P_N K_S/P_A^2)}{\ln\left[1\Big/\left\{1+(Z^A-Z^N)\Big(\frac{1}{P_A}\Big)\Big(\frac{dP_A}{dZ^A}\Big)\right\}\right]}.\qquad(9)$$

On the other hand, combining Eqs. (5. b) and (6. b), whether the ammonia adsorption is allowed for or not, yields another ν_r expression in common,

$$\nu_r = \frac{\ln (P_H^3 P_N K_S/P_A^2)}{\ln\left\{1+(Z^A-Z^N)\Big(\frac{1}{2P_N}\Big)\Big(\frac{dP_A}{dZ^N}\Big)\right\}}.\qquad(10)$$

The above three expressions for ν_r are also given in a previous paper[2]. In order to analyze the experimental data reported herein, it is necessary to add one more ν_r expression which is derived by eliminating Z^A from Eq. (10). Since the N^{15}-atomic fraction averaged over ammonia and nitrogen is regarded as constant in the course of the reaction,

$$Z^A P_A' + 2Z^N P_N = Z_i'(P_A' + 2P_N),\qquad(11)$$

where Z_i' is the particular value of Z^A or Z^N in exchange equilibrium of N^{15}-atoms. Inserting Z^A from Eq. (11) into (10),

$$\nu_r = \frac{\ln (P_H^3 P_N K_S/P_A^2)}{\ln\left\{1+(Z_i'-Z^N)\Big(\frac{1}{P_A'}+\frac{1}{2P_N}\Big)\Big(\frac{dP_A}{dZ^N}\Big)\right\}}.\qquad(12)$$

1. 3. Quasi-Equilibrium. The ammonia synthesis reaction (2) is assumed to consist of three steps:

$$N_2 = 2N(a) \qquad\qquad (13.\ I\ )$$

$$H_2 = 2H(a) \qquad\qquad (13.\ II\ )$$

$$3H(a)+N(a) = NH_3. \qquad\qquad (13.\ III)$$

Since step (13. II) is accepted as extremely fast, step (13. I) or (13. III) must

be rate-determining, depending upon which step is in quasi-equilibrium. In order to make this determination, two diagnostic quantities ϕ and ψ have previously[1] been introduced :

$$\phi \equiv (Z_1^N)^2/Z_0^N Z_2^N K_N, \tag{14}$$

where Z_0^N, Z_1^N, and Z_2^N are the mole fractions of N_2^{14}, $N^{14}N^{15}$, and N_2^{15} respectively in gas phase nitrogen, and K_N is the equilibrium constant ($=4$) for nitrogen isotope equilibration, $N_2^{14} + N_2^{15} = 2N^{14}N^{15}$, and

$$\psi \equiv 2(1-Z^A) \, dZ_2^N/Z^A dZ_1^N. \tag{15}$$

It has been demonstrated that if step (13. I) is in quasi-equilibrium, ϕ approaches unity and ψ approaches zero. Conversely, if step (13. III) is in quasi-equilibrium, ϕ should be close to zero and ψ close to unity. The criterion based on ϕ is valid for both ammonia synthesis and decomposition except in their initial and final stages, and the criterion based on ψ is applicable to the initial stage of the decomposition.

2. Experimental

Since the experimental procedures are similar to those detailed in the first paper[1] of this series, it is only necessary to repeat them very briefly with special reference to some of the modifications employed.

2. 1. Apparatus. The glass apparatus previously used was modified : the attached gas pipettes, GP_1 (95.4 mℓ) and GP_2 (108.9 mℓ), were replaced by smaller ones GP_3 (68.41 mℓ) and GP_4 (54.84 mℓ) to save more reaction gas. Each of the new pipettes was connected directly to the reaction system through a stopcock so that the two pipettes could be filled with one or two sample gases. When the reactions were conducted at pressures above atmospheric, a special device (Fig. 1) was attached to each stopcock in the reaction system to keep the male and female parts tight together against the inside pressure.

2. 2. Materials. The hydrogen, nitrogen, and $N^{15}H_3$ used were prepared as previously noted. The $N^{15}H_3$ was prepared from two ammonia sulfate samples, which were purchased from Rikagaku Kenkyusho (The Institute of Physical and Chemical Research) and were stated to be 96 and 99 N^{15}-atomic percent. The singly-promoted iron catalyst was from the same preparation used before[1]. A weighed sample of the catalyst (0.32 g of 30–40 mesh) was placed in the reaction vessel, and reduced for 72 hrs at 450°C. During the reduction, the hydrogen pressure was maintained between 54 and 55
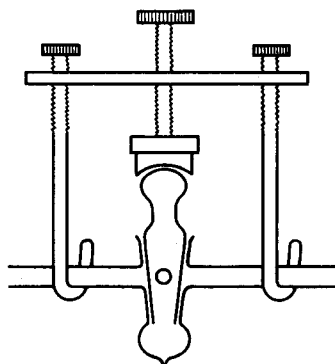

Fig. 1. Device to keep the male and female parts of a stopcock tight together under pressure.

cmHg.

2. 3. General Procedures. The first eight runs listed in Table 1 were carried out successively without renewing the catalyst. Between runs the catalyst was evacuated for 3 hours at 400°C. After these experiments, a blank run (run 9) was made using no catalyst. Measurements were made of ν_r, ϕ, and ψ at the desired higher temperatures in runs 1, 2, 5, 6, and 7 in which the total pressure was set at 850 mmHg instead of the 550 mmHg previously used. This higher total pressure was required to keep the equilibrium pressure of ammonia at the same level as that in the previous work[1] since ν_r measurements at lower ammonia pressures have been found to be inaccurate. For a comparison of catalyst activity, in run 4 the reaction temperature and total pressure were set to the same as those previously used[1], and in runs 3 and 8 to the same as those used by ENOMOTO and HORIUTI[3]. In the latter two runs neither tracer nor ammonia was used in the starting reaction mixture.

TABLE 1. Reaction conditions

Run	Catalyst	Reaction	Temp. (°C)	Pressure (mmHg) total	ammonia (initial)	(final)	Remarks
1		decompn.	390	850	11.7	4.3	
2		syn.	390	850	1.9	4.3	
3	0.32 g of singly-promoted iron (Fe–Al₂O₃)	syn.	400	404	0.0	0.8	No tracer
4		decompn.	340	550	9.1	3.9	
5		decompn.	360	850	12.0	7.2	
6		syn.	360	850	2.7	7.0	
7		decompn.	390	850	17.6	5.1	
8		syn.	400	404	0.0	0.9	No tracer
9	None	decompn.	390	850	14.2	14.0	No tracer

During the reaction the rate of circulation of the reaction mixture was regulated so as to develop a constant pressure across the ends of the constricted tube of the flow meter attached to the circulation loop (Fig. 1, ref. 1). The constricted tube was 2.36 cm long and 0.878 mm in inner diameter. The developed pressure was read on the flow meter as the difference in height of the oil columns, the density of the oil being 0.902. The flow rate was adjusted to give a pressure of 3.0 cm of oil for runs 3 and 8, 3.5 cm of oil for run 4, and 4.0 cm of oil for the other runs*).

2. 4. Analytical Procedures. The partial pressures P_H, P_N, and P_A were measured with manometers. In runs 1 and 2, isotopic analyses were made with a Hitachi RMU–5B mass spectrometer using the procedures previously described. An improved technique was used for the other runs on a Hitachi RMU–6 mass spectrometer. Previously, ammonia samples were analyzed directly in the mass spectrometer. To minimize any possible memory

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*) In a previous work (reference 1), the regulated pressure was 3.5 cm of oil for all the runs conducted, with the same flow meter.

effect, the ammonia sample was allowed to leak into the mass spectrometer for about ten minutes just before the data were taken. Control experiments showed that even with this precaution the spectral data were not always free from memory effect. In the improved method, this difficulty was overcome by oxidizing the ammonia with sodium hypobromite[11,12] and admitting the resulting nitrogen gas to the mass spectrometer. Peaks were measured at m/e 28, 29 and 30 and Z^A was evaluated from the data. Fig. 2 shows the Rittenberg tubing with two small bulbs used for oxidation. One of the bulbs was partly filled with 0.5 cc of an alkali solution of sodium hypobromite and the other with 0.5 cc of 0.25 N hydrochloric acid. The Rittenberg tubing was then connected to the analyzing system (Fig. 4, reference 1) in place of the sample vessel SV$_2$, and pumped off by a repeated freeze-evacuate-thaw technique. An ammonia sample was introduced into the

Fig. 2.
Rittenberg tubing

HCl bulb by means of liquid nitrogen. The Rittenberg tubing was then disconnected from the vacuum line, allowed to stand until the solid melted away, and then tilted to bring the two solutions together for ammonia oxidation.
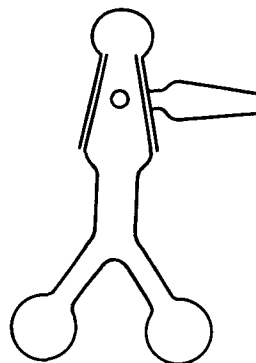
In runs 1 and 2, the mass spectral analysis of nitrogen gas was made by directly feeding a sample mixture of hydrogen and nitrogen into the mass spectrometer. Three peaks were measured at m/e 28, 29 and 30 to evaluate Z^N. With this method the presence of hydrogen presented some difficulties, the ratio of peaks at m/e 29 to 28 being dependent upon sample pressure. In the improved technique used in the other runs, the hydrogen was separated from the sample mixture by admitting the mixture by means of liquid nitrogen to a vessel containing synthetic type 13X zeolite. When the liquid nitrogen trap was replaced by an acetone slurry bath ($-94°C$), the hydrogen was released and most of the nitrogen remained adsorbed on the zeolite. The hydrogen was removed by repeated expansions outside of the vessel, and then the adsorbed nitrogen was evaporated by warming the vessel to room temperature. The pure nitrogen sample thus prepared was led into the mass spectrometer. In this improved technique, the observed ratio of m/e 29 to 28 remained essentially constant for a sample pressure.

3. Results and Discussion

The manometric and mass spectral data obtained are presented in the first section (3.1). Sections 3.2 to 3.5 deal with the equilibrium constant, the catalytic activity, the ammonia adsorption *etc.*, on the basis of the observed data. These quantities are related to the reliability of the evaluation of ν_r, and some of them may suggest an explanation for the conflicting results between ENOMOTO and HORIUTI[3] and the present authors. Numerical calculations for ν_r *etc.* are given in the last two sections (3.6 and 3.7).

3.1. Manometric and Mass Spectral Data. The data obtained are

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TABLE 2. The manometric and mass spectral data for ammonia synthesis and decomposition and for N^{15}-exchange

Run	Sample	t (hr)	P_A (mmHg)	Z^A	Z_1^N	Z_2^N	Z^N	V_t (1)	$\dfrac{a_{(s)}RT}{V_t}$ (mmHg)	$P_A + \dfrac{a_{(s)}RT}{V_t}$ (mmHg)
1	0	0	11.65	0.947			0.00365			12.27
								1.818	0.62	
	1	0.5	10.26	—	(0.0095)	(0.0042)	(0.0090)			10.88~10.90
								1.770	0.64	
	2	3	6.36	—	0.0104	0.0120	0.0172			7.00~ 7.01
								1.727	0.65	
	3	6.1	4.55	0.575	0.0167	(0.0163)	(0.0247)			5.20~ 5.22
								1.672	0.67	
	4	9.5	4.26	0.278	0.0208	0.0183	0.0287			4.93~ 4.96
								1.605	0.70	
	5	14	4.29	0.177	(0.0264)	(0.0176)	(0.0308)			4.99~ 5.02
								1.538	0.73	
	6	22	4.30	0.139	(0.0266)	0.0172	(0.0305)			5.03~ 5.07
								1.466	0.77	
	7	27	4.29	0.098	—	—	—			5.06
	∞		4.3	0.0317			0.0317			
2	0	0	1.87	0.878	—	—	0.00365			2.37
								2.127	0.50	
	1	0.5	2.53	0.540	0.0080	0.0006	0.0046			3.03~ 3.06
								2.010	0.53	
	2	2	3.53	0.296	0.0090	(0.0011)	(0.0056)			4.06~ 4.10
								1.881	0.57	
	3	4	4.31	0.164	0.0114	0.0011	0.0068			4.88~ 4.92
								1.760	0.61	
	4	7	4.23	0.090	0.0118	(0.0013)	(0.0072)			4.84~ 4.89
								1.634	0.66	
	5	10	4.38	0.043	(0.0167)	0.0007	(0.0091)			5.04~ 5.09
								1.517	0.71	
	6	14	4.26	0.029	0.0131	(0.0007)	(0.0073)			4.97~ 5.00
								1.443	0.74	
	7	22.5	4.34	0.029	0.0166	0.0007	0.0090			5.08~ 5.12
								1.377	0.78	
	8	26	4.32	0.020	0.0144	(0.0008)	(0.0080)			5.10
	∞		4.3	0.0088			0.0088			
3	0	0	0.01							
								2.220		
	1	0.3	0.47							
								2.100		
	2	1.5	0.79							
								1.967		
	3	4.0	0.79							
								1.846		
	4	7.0	0.79							
4	0	0	9.12	—	—	—	0.00365			9.65
								2.122	0.53	
	1	0.5	8.46	0.937	0.0077	0.0002	0.0041			8.99~ 9.01
								2.056	0.55	
	2	2	7.86	0.927	0.0083	0.0010	0.0052			8.41~ 8.43
								1.989	0.57	
	3	7	7.55	0.909	0.0082	0.0041	0.0082			8.12~ 8.14
								1.918	0.59	
	4	16	6.53	0.855	0.0098	0.0086	0.0135			7.12~ 7.14
								1.855	0.61	
	5	24	5.86	0.801	0.0111	0.0121	0.0177			6.47~ 6.49
								1.799	0.63	
	6	32	5.00	0.720	0.0121	0.0142	0.0203			5.63~ 5.65
								1.726	0.65	
	7	40	4.70	0.631	0.0146	0.0164	0.0237			5.35~ 5.38
								1.656	0.68	
	8	48	4.39	0.532	0.0165	0.0190	0.0273			5.07~ 5.10
								1.590	0.71	
	9	56	4.20	0.440	0.0186	0.0184	0.0277			4.91~ 4.94
								1.520	0.74	
	10	64	3.91	0.353	0.0211	0.0199	0.0305			4.65~ 4.68
								1.454	0.77	
	11	73	3.95	0.278	0.0229	0.0198	0.0313			4.72~ 4.76
								1.388	0.81	
	12	80	3.92	—	0.0251	0.0203	0.0329			4.73~ 4.77
								1.319	0.85	
	13	88	3.88	0.191	0.0266	0.0204	0.0337			4.73
	∞		3.8	0.0351			0.0351			
5	0	0	11.97	—	—	—	0.00365			12.54
								2.045	0.57	
	1	0.5	11.74	—	0.0076	0.0000	0.0038			12.31~12.33
								1.983	0.59	
	2	2.5	11.61	—	0.0080	0.0010	0.0050			12.20~12.22
								1.909	0.61	
	3	5	11.57	—	0.0077	0.0014	0.0053			12.18~12.20
								1.849	0.63	

The Rate-Determining Step of Ammonia Synthesis and Decomposition

5	4	18	10.64	—	0.0082	0.0040	0.0081	1.779	0.65	11.27~11.29
	5	29	10.18	—	—	—	—	1.713	0.68	10.83~10.86
	6	36	9.86	—	0.0091	0.0069	0.0115	1.647	0.71	10.54~10.57
	7	47	9.54	—	0.0094	0.0083	0.0130	1.572	0.74	10.25~10.28
	8	60	9.05	—	0.0115	0.0101	0.0159	1.507	0.77	9.79~9.82
	9	80	8.50	—	0.0120	0.0120	0.0180	1.442	0.81	9.27~9.31
	10	102	8.10	—	0.0141	0.0135	0.0206	1.374	0.85	8.91~8.95
	11	135	7.43	—	0.0175	0.0154	0.0242	1.305	0.89	8.28~8.32
	12	168	7.29	—	0.0200	0.0168	0.0268	1.232	0.94	8.18~8.23
	13	206	7.21	—	0.0225	0.0160	0.0273			8.15
	∞		7.1							
6	0	0	2.66	0.920	—	—	0.00365			3.14
	1	0.5	2.72	0.846	0.0074	0.0000	0.0037	2.247	0.48	3.20~3.23
	2	4	3.22	0.716	0.0072	0.0002	0.0038	2.129	0.51	3.73~3.76
	3	7	3.68	0.621	0.0078	0.0004	0.0043	2.001	0.54	4.22~4.26
	4	12	4.14	0.536	0.0088	0.0005	0.0049	1.878	0.58	4.72~4.76
	5	21	5.04	0.438	0.0097	0.0007	0.0056	1.755	0.62	5.66~5.71
	6	33	5.71	0.314	—	—	—	1.627	0.67	6.38~6.41
	7	47	6.25	0.235	0.0123	0.0015	0.0077	1.563	0.70	6.95~6.98
	8	61	6.45	0.193	0.0125	0.0010	0.0073	1.491	0.73	7.18~7.22
	9	80	6.83	0.136	0.0146	0.0016	0.0089	1.418	0.77	7.60~7.64
	10	104	6.85	0.086	0.0160	0.0017	0.0097	1.349	0.81	7.66~7.69
	11	135	6.96	0.079	0.0169	0.0013	0.0098	1.291	0.84	7.80
	∞		7.1	0.0108			0.0108			
7	0	0	17.56	0.961	—	—	0.00365			18.14
	1	0.25	17.10	0.952	0.0074	0.0010	0.0047	1.965	0.58	17.68~17.70
	2	0.75	16.81	0.949	0.0078	0.0024	0.0063	1.897	0.60	17.41~17.43
	3	1.5	16.12	0.946	0.0079	0.0037	0.0077	1.847	0.62	16.74~16.77
	4	3	15.12	0.939	0.0080	0.0063	0.0103	1.771	0.65	15.77~15.78
	5	5	13.70	0.928	0.0086	0.0095	0.0138	1.732	0.66	14.36~14.39
	6	9	11.19	0.885	0.0091	0.0156	0.0202	1.666	0.69	11.88~11.90
	7	15.5	8.80	0.814	0.0117	0.0215	0.0274	1.613	0.71	9.51~9.54
	8	20	7.64	0.750	0.0131	0.0235	0.0301	1.545	0.74	8.38~8.41
	9	29	6.37	0.609	0.0164	0.0267	0.0349	1.477	0.77	7.14~7.18
	10	39	5.50	0.450	0.0194	0.0285	0.0382	1.412	0.81	6.31~6.35
	11	55	5.05	0.260	0.0238	0.0288	0.0407	1.342	0.85	5.90~5.94
	12	72	5.08	0.157	0.0270	0.0295	0.0430	1.286	0.89	5.97
	∞		4.3	0.0441			0.0441			
8	0	0	0.00					2.232		
	1	0.5	0.47					2.109		
	2	1.5	0.81					1.988		
	3	4	0.90					1.857		
	4	7	0.92					1.749		
	5	10	0.91							
9	0	0	14.20					1.993		
	1	1	13.90					1.927		
	2	4.2	13.94					1.855		
	3	9	14.02							

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presented in Table 2. The variation in the volume of the reaction system V_i (S_R in Fig. 1, reference 1) are also included. The volume decreased stepwise with each sampling, but remained essentially constant between
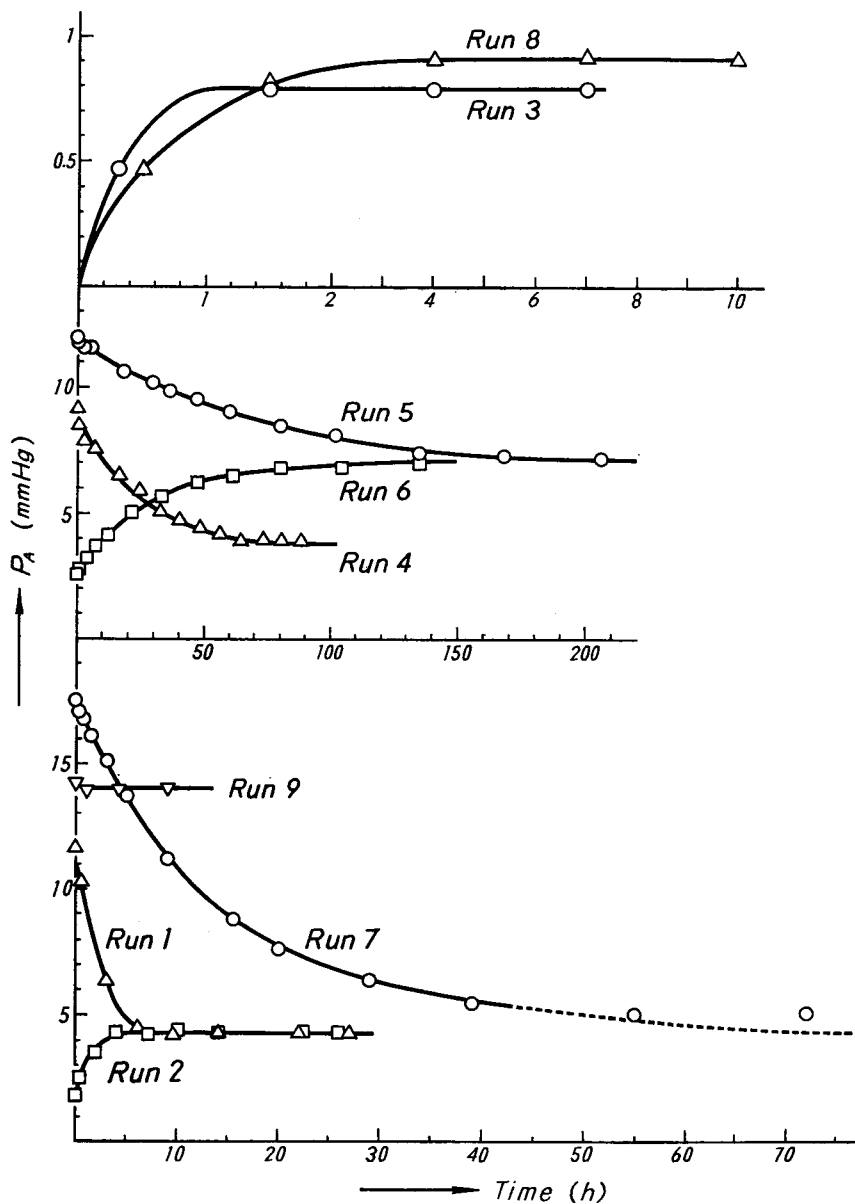

Fig. 3. Pressure of ammonia plotted against time.

samplings. The mass spectral data enclosed in parentheses are less accurate, and were not used in the later numerical calculations for ν_r. The Z^N value for the samples numbered 0 was taken as 0.00365, the generally accepted natural abundance, since the mass spectral analyses were not very accurate for nitrogen gas samples close to the natural abundance values. The last two columns are explained in Section 3.4, and the calculations for Z^A or Z^N at $t=\infty$, *i.e.* Z'_t, are given in Section 3.5.

3.2. Equilibrium Constant and Heat of Reaction. Fig. 3 shows the observed $P_A \sim t$ profiles[*], from which $(P_A)_e$, the equilibrium pressure of ammonia, may be estimated as 4.3 ± 0.1 mmHg for runs 1, 2 and 7 (390°C) and as 7.1 ± 0.1 mmHg for runs 5 and 6 (360°C). Table 3 gives the equilibrium constant K_S (for $3H_2+N_2=2NH_3$) and the heat of reaction Q_P calculated from these $(P_A)_e$ values. Values from other sources are also included for a comparison. It should be noted that the equilibrium constants obtained by the present authors as well as those obtained by ENOMOTO and HORIUTI were appreciably lower than would be expected from HABER's formula[15].

TABLE 3. Equilibrium constant and heat of reaction

Temp. (°C)	K_S (mmHg^{-2})	Q_P (kacl/mole)	K_S	Q_P	K_S	Q_P
305	53.4×10^{-10}	} 25.1	69.9×10^{-10}	} 24.7		
340	15.4×10^{-10}		$20.3 \times$ „			
360	$(9.47\pm0.27)\times10^{-10}$	} 28.2	$10.7 \times$ „	} 25.2		
390	$(3.43\pm0.16)\times10^{-10}$		$4.33 \times$ „			
400			$3.27 \times$ „	} 25.5	1.86×10^{-10}	} 29.6
430			$1.45 \times$ „		$0.724\times$ „	
445			$0.996\times$ „		$0.572\times$ „	
450			$0.876\times$ „		$0.560\times$ „	
Source	Present and previous work (ref. 1)		HABER's formula (ref. 15)		ENOMOTO and HORIUTI (ref. 3)	

3.3. Catalyst Activity. As is shown in Fig. 3 there was a marked difference in catalyst activity between runs 1 and 7 and between runs 3 and 8 despite common reaction conditions. This variation in catalyst activity is

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[*] These $P_A \sim t$ profiles and those given in reference 13 are based on the same data but different time scales are used. In the profiles given here the actual reaction time is used in place of the hypothetical reaction time for reference 13. The definition of the hypothetical time was given in reference 14.

probably attributable to the very small amount of catalyst used, which may be extremely sensitive to any trace of possible impurity such as water vapor and carbon monoxide.

A comparison of catalyst activity in the present work with that of ENOMOTO and HORIUTI's[3] may be made on the basis of the time (t) required for the hydrogen-nitrogen mixture to yield a certain fraction of ammonia. With any reaction mixture involved in a closed system with a catalyst, t is expected to be proportional to the volume of the system (V) and inversely proportional both to the catalyst weight (W) and to the catalyst activity per unit weight (A). This relation may be formulated for the reaction systems used by the present authors and by ENOMOTO and HORIUTI, indicated by the suffixes t and e respectively,

$$t_t = k_t V_t / W_t A_t \qquad (16.\,t)$$

$$t_e = k_e V_e / W_e A_e. \qquad (16.\,e)$$

The two constants k_t and k_e become identical if the same reaction conditions except for V, W and A are used for both systems. Thus we have

$$\frac{A_t}{A_e} = \frac{V_t t_e W_e}{V_e t_t W_t}. \qquad (17)$$

One of ENOMOTO and HORIUTI's experiments was run at 400°C and a total pressure of 404 mmHg, started with a 3:1 hydrogen-nitrogen mixture[*] (Table II, reference 3). As was mentioned in Section 2.3, these conditions were reproduced in runs 3 and 8 of the present work to allow a comparison of catalyst activities on the basis of Eq. (17). In ENOMOTO's run, V_e and W_e were 5.2 liters[**] and 23 g, and t_e was 265 min $\simeq$ 4.4 hr in going from $P_A = 0.440$ to 0.654 mmHg. These P_A values correspond to $P_A/(P_A)_e$ values of 0.595 and 0.884, $(P_A)_e$ being taken as 0.74 mmHg (Table III, reference 3). In the present work, on the other hand, $V_t = 2.0 \pm 0.2$ liters, $W_t = 0.32$ g, and t_t is taken from Fig. 3 as 0.36 hrs (run 3) and 0.84 hrs (run 8) for the same $P_A/(P_A)_e$ range as that used for the t_e evaluation. Inserting these values into Eq. (17) we obtain

$$A_t/A_e = (3.4 \pm 0.4) \times 10^2 \text{ for run } 3$$
$$= (1.5 \pm 0.2) \times 10^2 \text{ for run } 8.$$

Comparison of run 4 in the present work with run 4 in a previous work[1]

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*) This mixture contained a small amount of ammonia.

**) This figure for the volume was derived from data given in their report: 2600 cc of reaction mixture at STP exerting a pressure of 404 mmHg in the reaction system, and an assumed room temperature of 20°C.

shows that the catalyst used here was approximately five times as active as the one previously used.

3. 4. Ammonia Adsorption. As previously pointed out[1], there are three different types of adsorption to be considered; ammonia adsorption on the glass walls (type G), ammonia adsorption on the catalyst (type C), and residual nitrogen or nitrogen containing species on the catalyst (type R). Table 4 lists the observed amounts of type G adsorption $(P_{A,calc.} - P_{A,obs.})$ expressed as the decrease in ammonia pressure due to adsorption. The ambient ammonia pressures $(P_{A,obs.})$ is also included. Although there is considerable scatter in the data, the pressure decrease appears essentially independent of ammonia pressure in accord with the previous results, suggesting the ammonia adsorption to saturation. The average decrease, 0.34 mmHg, is also in close agreement with the previous value, 0.32 mmHg.

As only a very small amount of catalyst was used, types C and R adsorptions were not observed clearly. However, the amounts of these adsorptions (a_C and n_R) could be estimated from the adsorption data in the

TABLE 4. Ammonia adsorption on the glass walls

Run	1	2	4	5	6	7	9	mean
$P_{A,obs.}$ (mmHg)	11.65	1.87	9.12	11.97	2.95	17.56	14.20	
$P_{A,calc.} - P_{A,obs.}$	0.40	0.21	0.50	0.37	0.32	0.37	0.18	0.34

TABLE 5. The amounts of adsorbed ammonia and residual nitrogen

Work	Run	a_G (μmole)	a_C (μmole)	n_R (μmole)	a_Σ (μmole)
Present	1	39	11	11	61
	2	"	8	"	58
	4	"	11	"	61
	5	"	13	"	63
	6	"	9	"	59
	7	"	12	"	62
Previous	3	37	35[a]	51	123
	4	"	50[a]	"	138
	5	"	45[a]	"	133
	6	"	60[a]	"	148

a) Estimated from Fig. 7 in reference 1.

previous work, where 1.51 g of catalyst was used as compared with 0.32 g in the present work, by assuming a direct proportion of the adsorptions to the catalyst weight and by allowing for the dependence of a_C on the ammonia pressure based on Fig. 7 of reference 1. The calculated values are listed in Table 5, where a_G is the average amount of type G adsorption converted into mole. The adsorption data from previous experiments are also tabulated for a comparison. The sum of a_G, a_C and n_R, denoted by a_Σ, may be approximated to $a_{(a)}$ in Eq. (8) and inserted into Eqs. (7) or (12) to calculate ν_r. The quantity $a_{(a)}RT/V_i$ in Eq. (8) or Table 2 could be interpreted as the total amount of the three adsorbed species expressed as the pressure which they would have exerted in the reaction system had they been released as gaseous ammonia. A comparison of P_A and $a_{(a)}RT/V_i$ shows that despite the very small size of the catalyst used the adsorbed ammonia is not negligible compared with the gas phase ammonia in synthesis runs 2 and 6.

3.5. Values for Z_i'. One must know Z_i' to calculate ν_r from Eq. (12). The Z_i' values calculated from Eqs. (8) and (11) are shown in Table 6. It is seen that during reaction Z_i' remained substantially unaltered although V_i decreased significantly. The Z_i' value averaged over all samples in a run was thus used for the later calculations of ν_r for that particular run.

TABLE 6. The values for Z_i'

| Sample	Run 1	Run 2	Run 4	Run 6	Run 7
1		0.0084	0.0341	0.0100	0.0433
2			0.0330	0.0100	0.0441
3		0.0086	0.0344	0.0104	0.0439
4	0.0316		0.0350	0.0108	0.0441
5			0.0359	0.0113	0.0442
6	0.0318		0.0344		0.0440
7		0.0093	0.0354	0.0114	0.0448
8			0.0365	0.0104	0.0442
9			0.0350	0.0111	0.0445
10			0.0359	0.0111	0.0443
11			0.0355	0.0111	0.0437
12					0.0446
13			0.0364		
Mean	0.0317	0.0088	0.0351	0.0108	0.0441
Standard deviation	0.0001	0.0004	0.0010	0.0005	0.0004
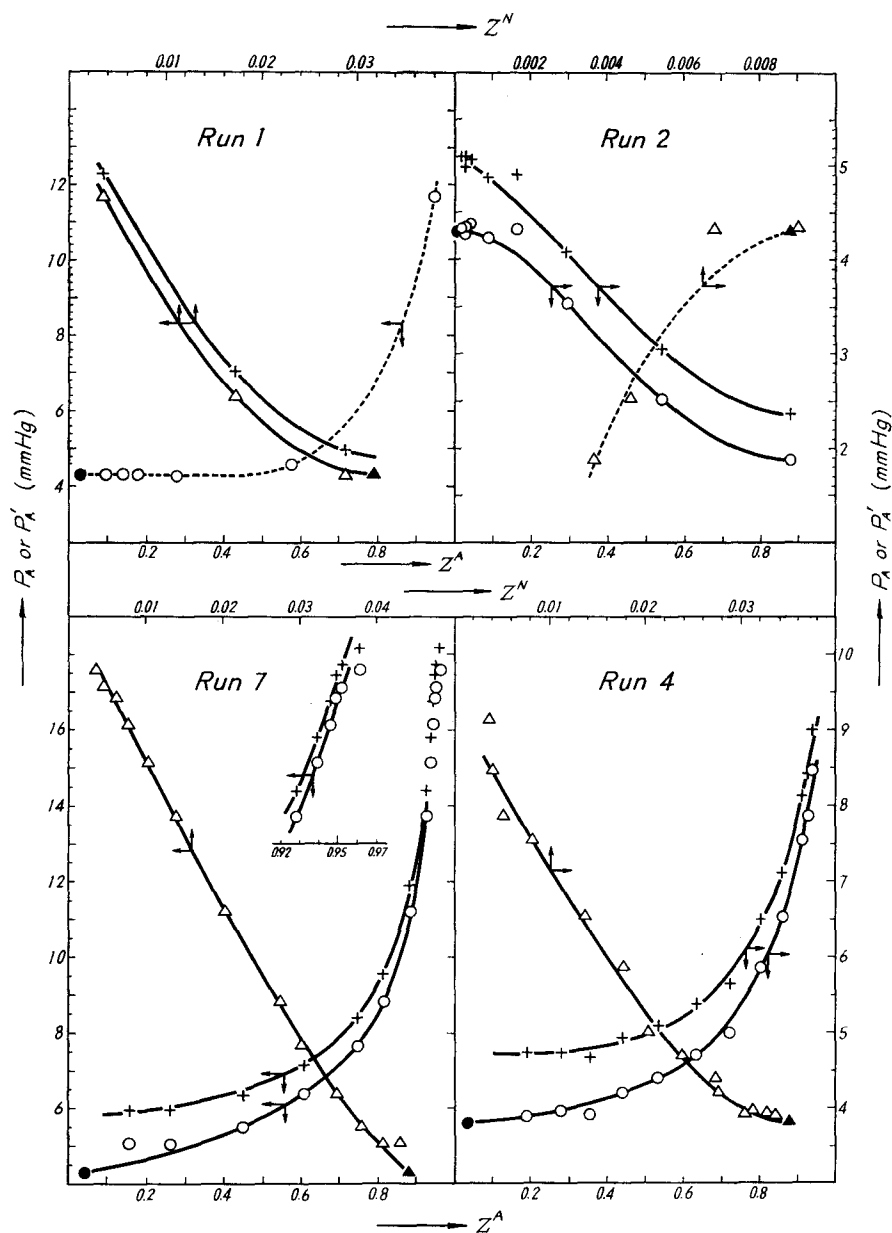
Fig. 4. Ammonia pressure plotted against N^{15}-atomic fraction of ammonia or of nitrogen : Runs at 340 and 390°C.

○, $P_A \sim Z^A$; +, $P'_A \sim Z^A$ or $P'_A \sim Z^N$; △, $P_A \sim Z^N$.

3.6. ν_r. Figs. 4 and 5 show part of the kinetic data given in Table 2. The directly observed values are plotted as open circles, open triangles or crosses, and the calculated equilibrium values as solid circles or solid triangles. The procedure for evaluating ν_r from these figures is illustrated using Eq. (7) and run 7. At a certain value of P_A, a horizontal line (parallel to Z^A axis) was drawn and the Z^N value was read at the intersection with the P_A vs. Z^N curve. The value for Z^A and its derivative dP_A/dZ^A were determined at the intersection with the P_A vs. Z^A curve, the derivative being taken as the slope of the tangent to the curve. A vertical line was then drawn through the latter intersection and the P_A' value was read at the resulting intersection of the vertical line and the P_A' vs. Z^A curve. The pressures P_H and P_N were determined using the relations $P_H = 3(P_T - P_A)/4$ and $P_N = (P_T - P_A)/4$, where P_T is the total pressure. The values thus obtained were all inserted into Eq. (7) to calculate ν_r. Calculations of this sort were repeated at a set of different P_A values for each run. The calculations for ν_r from Eqs. (9), (10) and (12) were made in a similar manner. The Table in Ap-
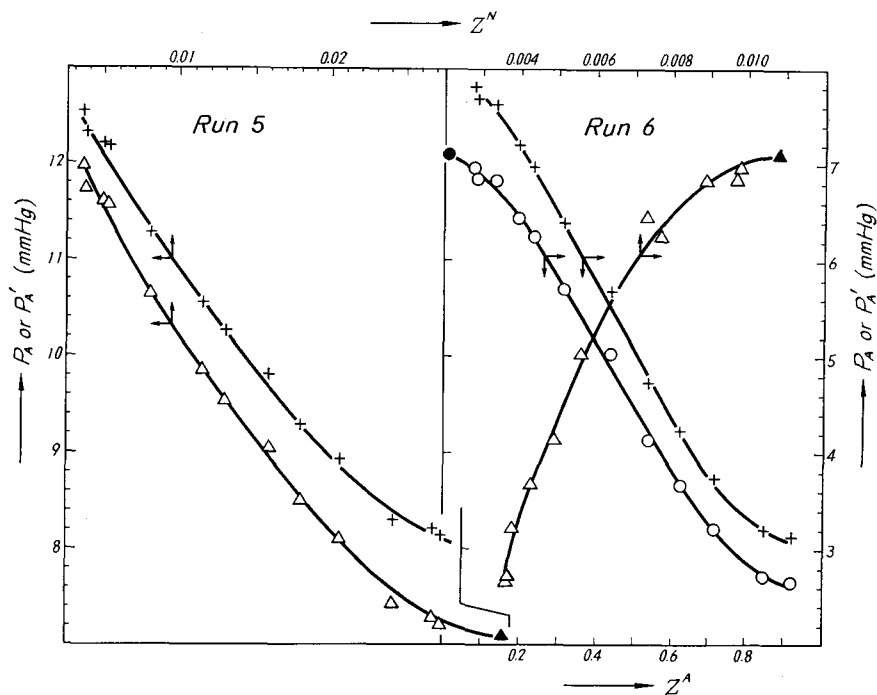

Fig. 5. Ammonia pressure plotted against N^{15}-atomic fraction of ammonia or of nitrogen: Runs at 360°C.

○, $P_A \sim Z^A$; +, $P_A' \sim Z^A$ or $P_A' \sim Z^N$; △, $P_A \sim Z^N$.

pendix lists the ν_r values thus calculated together with their probable errors, the calculations for which are also described in the Appendix. In Figs. 6 and 7 some of the ν_r data are plotted against chemical affinity to depict a general trend. The probable errors are indicated by the heights of the vertical bars.

In most decomposition runs (1, 4 and 5), the obtained ν_r values are closer to one than to two over the chemical affinity range studied, suggesting that nitrogen desorption (step 13. I) is rate-determining. In the other decomposition run (7), at first glance, ν_r appears to increase with decreasing P_A, and ultimately to approach a value of two or even higher. However, as shown in Fig. 3, in this run, $(P_A)_e$ seems close to 5 mmHg rather than to 4.3 mmHg, the latter $(P_A)_e$ value being used to evaluate ν_r for all 390°C runs. Calculations revealed that raising $(P_A)_e$ from 4.3 to 5 mmHg in this particular run decreases ν_r to near unity over the P_A region studied. Thus, the results of run 7 might well be interpreted as indicating that ν_r is unity in accord with the results of the other decomposition runs. No explanation can now be given to the apparent $(P_A)_e$ shift from 4.3 to 5 mmHg. In runs
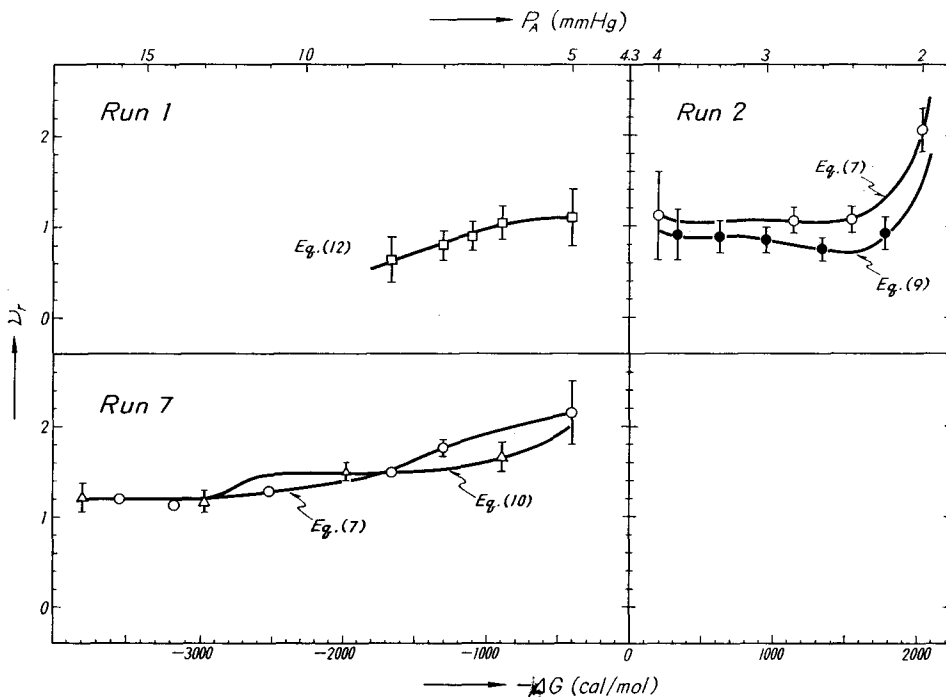

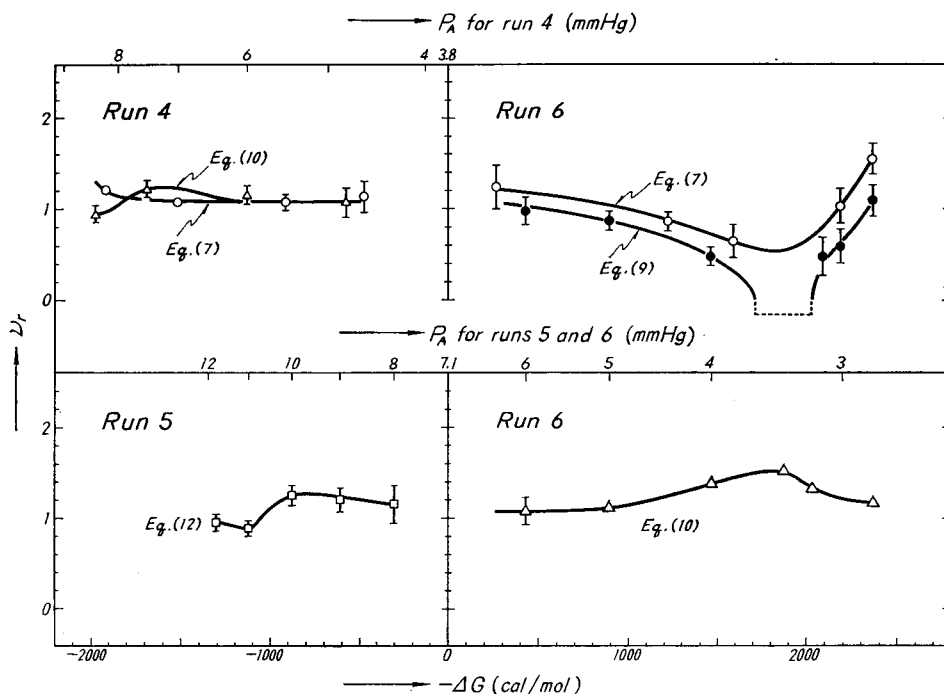**Fig. 6.** Observed ν_r values and their probable errors as a function of chemical affinity: Runs at 390°C.

Fig. 7. Observed ν_r values and their probable errors as a function of chemical affinity: Runs at 340 and 360°C.

4 and 7, the ν_r values obtained from Eq. (7) are in good agreement with those from Eq. (10).

In the decomposition runs, there is no doubt that the ν_r value was one, but unexpectedly peculiar ν_r profiles were observed on the synthesis side. Fig. 6 shows that in run 2 the ν_r value, whether calculated from either Eq. (7) or (9), was close to two in the initial reaction stage, decreased rapidly to a minimum with decreasing chemical affinity, and then finally increased very slowly approaching a value close to one. The same tendency was even more pronounced in run 6 as shown in Fig. 7. The minimum value for ν_r, when calculated from Eq. (7), fell around 1800 cal of $-\Delta G$. The ν_r profile calculated from Eq. (9) was almost parallel to that calculated from Eq. (7), but did not give any meaningful ν_r values in the neighborhood of the minimum as the term $1/\{1+(Z^A-Z^N)(1/P_A)(dP_A/dZ^A)\}$, was negative in that region. It is also curious that in run 6 the ν_r value derived from Eq. (10) is at a maximum right in the $-\Delta G$ region where the ν_r value obtained using Eq. (7) or (9) is at a minimum. In the low $-\Delta G$ region near equilibrium, however, the three ν_r expressions all yielded ν_r values close to unity,

thus suggesting that nitrogen chemisorption is rate-determining. It is to be noted that the unexpectedly peculiar ν_r profilies were observed only in the higher $-\Delta G$ region where P_A was very low. When values for P_A are low, the ammonia adsorption must be treated very precisely to obtain accurate values for ν_r. There is no guarantee that the ν_r expression (7) is precise enough to meet this requirement for the low P_A region. It is still questionable whether the peculiar maximum and minimum for ν_r really reflect a certain change in the reaction mechanism or whether they are deceptive because of the inaccurate treatment of ammonia adsorption. In this connection it may be worth citing TEMKIN's work[16] which suggests that when P_A is far below the equilibrium pressure the overall reaction of ammonia synthesis is controlled by two steps (13. I) and (13. III). More detailed and accurate investigation should be undertaken on the synthesis side.

In summary the observed ν_r values of one, coupled with the ϕ and ψ values in Section 3.7, present sufficient evidence for step (13. I) being rate-determining, except in the region where the ammonia pressure is much lower than the equilibrium value. This is to be contrasted with the results obtained by ENOMOTO *et al.* showing that $\nu_r = 2$, and suggesting that step (13. III) is rate-determining. There is still the difference in reaction temperature used, *i.e.* 390°C and down in the present study and 430°C in ENOMOTO and HORIUTI. However, it does not seem logical to suppose that the rate-determining step would change or that the ν_r value would increase from one to two just by going from 390 to 430°C. It is probably more likely that the difference in ν_r may be attributable to the striking difference in catalyst activity discussed in Section 3.3. Since the catalyst used by ENOMOTO and HORIUTI was much less active than that used in the present study, the former catalyst may have been poisoned in one way or another producing a preferential slowing in step (13. III) which resulted in a ν_r value of two. Alternatively, a lack of correction for ammonia adsorption might have given rise to erroneous ν_r values. Since ENOMOTO and HORIUTI did not observe any adsorption when measuring ν_r, it might be desirable to check the reproducibility of their results with special reference to adsoption.

3.7. **ψ and ϕ.** The results obtained have been previously[13] described in detail. It is worth repeating that both the ϕ and ψ values observed, in accord with ν_r, lend support to the view that nitrogen chemisorption and desorption are rate-determining. It should be particularly emphasized that there were no contradictions in the conclusion derived from the ϕ and ψ values as there were in the unexpected peculiarity in ν_r on the synthesis side.

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Acknowledgment

Appendix

Since ν_r is not measured directly but calculated from a set of different measurements, it is desirable to consider how errors in individual measurements may propagate to yield an error in the final ν_r value. The ν_r expressions used, (7), (9), (10) and (12), may be simplified by dropping any terms which are negligible for the purpose of error calculations. The numerator $\ln(P_H^3 P_N K_S / P_A^2)$ common in all the expressions is almost identical with $\ln\{(P_A)_e/P_A\}^2$, where $(P_A)_e$ is the equilibrium pressure of ammonia, since the variations in P_H and P_N in the present experiments are very small. Both $1/P_A'$ in Eq. (7) and $(1/P_A')+(1/2P_N)$ in Eq. (12) may be approximated by $1/P_A$. The ν_r expressions (7), (9) and (12) are then reduced to a common form,

$$\nu_r = \frac{\ln(B/A)^2}{\pm\ln\{1+(ZD/A)\}} ,\tag{i}$$

where the abbreviated notations are used: A for P_A, B for $(P_A)_e$, Z for $Z^A - Z^N$ or $Z_t' - Z^N$, and D for dP_A/dZ^A or dP_A/dZ^N. The other ν_r expression (10) may also be rewritten in a simplified form,

$$\nu_r = \frac{\ln(B/A)^2}{\ln\{1+(ZD/2N)\}} ,\tag{ii}$$

where N is the abbreviation for P_N.

Let us denote the errors in measurements of A, B etc. by e_A, e_B etc. On assuming that these errors are independent, the error in the final ν_r may be given as

$$E_\nu = \sqrt{\left(\frac{\partial\nu_r}{\partial B}\right)^2 e_B^2 + \left(\frac{\partial\nu_r}{\partial A}\right)^2 e_A^2 + \cdots\cdots} .\tag{iii}$$

Differentiating Eq. (i) partially with respect to each variable involved and inserting it into Eq. (iii) leads to

$$E_\nu = \frac{\alpha}{\beta}\sqrt{\frac{4}{\alpha^2}\left\{\left(\frac{e_B}{B}\right)^2 + \left(\frac{e_A}{A}\right)^2\right\} + \frac{1}{\beta^2}\left\{\frac{ZD/A}{1+(ZD/A)}\right\}^2} \\ \overline{\left\{\left(\frac{e_A}{A}\right)^2 + \left(\frac{e_Z}{Z}\right)^2 + \left(\frac{e_D}{D}\right)^2\right\} - \frac{4}{\alpha\beta}\left\{\frac{ZD/A}{1+(ZD/A)}\right\}\left(\frac{e_A}{A}\right)^2} ,\tag{iv}$$

where α and β represent $\ln(B/A)^2$ and $\pm\ln\{1+(ZD/A)\}$ respectively. Similarly Eq. (ii) yields

$$E_\nu = \frac{\alpha}{\gamma}\sqrt{\frac{4}{\alpha_2}\left\{\left(\frac{e_B}{B}\right)^2 + \left(\frac{e_A}{A}\right)^2\right\} + \frac{1}{\gamma^2}\left\{\frac{ZD/2N}{1+(ZD/2N)}\right\}^2\left\{\left(\frac{e_Z}{Z}\right)^2 + \left(\frac{e_D}{D}\right)^2 + \left(\frac{e_N}{N}\right)^2\right\}} ,\tag{v}$$

The Rate-Determining Step of Ammonia Synthesis and Decomposition

TABLE.　The data used for ν_r and E_ν evaluations

Run	P_A (mmHg)	P'_A (mmHg)	Z_A	Z^N	$\frac{dP_A}{dZ^A}$ (mmHg)	$\frac{dP_A}{dZ^N}$ (mmHg)	$-\Delta G$ (cal)	δRT[a] (cal) (by Eq.(7))	ν_r	E_ν	δRT[a] (cal) (by Eq.(9))	ν_r	E_ν	δRT[a] (cal) (by Eq.(10) or (12))	ν_r	E_ν
1	8.4	9.10		0.0111		−399	−1791							−3379	0.53	0.67
	8	8.69		0.0122		−378	−1660							−2650	0.63	0.25
	7.5	8.17		0.0135		−349	−1486							−2074	0.72	0.18
	7	7.68		0.0150		−323	−1301							−1656	0.79	0.16
	6.5	7.13		0.0167		−286	−1104							−1247	0.89	0.16
	6	6.65		0.0186		−239	−889							−858	1.04	0.18
	5.5	6.11		0.0209		−207	−657							−611	1.08	0.22
	5	5.59		0.0235		−163	−402							−366	1.10	0.31
2	1.96		0.762	0.004		−1.45	2086	781	2.67	0.30	1085	1.92	0.30			
	2		0.737	0.004		−1.80	2033	983	2.07	0.24	1421	1.43	0.24			
	2.2		0.644	0.004		−2.63	1780	1271	1.40	0.18	1909	0.93	0.18			
	2.4		0.576	0.004		−3.40	1549	1436	1.08	0.14	2191	0.71	0.14			
	2.6		0.519	0.005		−3.75	1337	1261	1.06	0.13	1782	0.75	0.13			
	2.8		0.467	0.005		−4.00	1140	1067	1.07	0.14	1421	0.80	0.14			
	3		0.418	0.005		−4.17	956	882	1.08	0.14	1125	0.85	0.14			
	3.2		0.369	0.005		−4.30	786	717	1.10	0.16	885	0.89	0.16			
	3.4		0.323	0.006		−4.43	624	581	1.07	0.18	703	0.89	0.18			
	3.6		0.278	0.006		−4.45	472	456	1.04	0.21	540	0.87	0.21			
	3.8		0.231	0.007		−4.10	331	313	1.06	0.28	365	0.91	0.28			
	4		0.177	0.007		−3.30	192	172	1.12	0.48	199	0.96	0.48			
4	9		0.943	0.0042										−2148		
	8.4	8.97	0.943	0.0042	24.8	−236	−1975	−1560	1.27	0.05	−1618	1.22	0.05	−2078	0.95	0.09
	8.2	8.73	0.936	0.0052	24.8	−236	−1914	−1576	1.21	0.05	−1632	1.17	0.05	−2030	0.94	0.09
	8	8.50	0.928	0.0061	24.8	−229	−1853	−1591	1.16	0.04	−1645	1.13	0.04	−1840	1.01	0.09
	7.5	8.05	0.908	0.0083	21.3	−205	−1691	−1484	1.14	0.05	−1546	1.09	0.05	−1388	1.22	0.09
	7	7.55	0.883	0.0109	19.1	−198	−1517	−1420	1.07	0.05	−1484	1.02	0.05	−1232	1.23	0.09
	6.5	7.10	0.854	0.0134	15.3	−199	−1333	−1260	1.06	0.06	−1330	1.00	0.06	−1165	1.14	0.09
	6	6.62	0.815	0.0160	11.35	−189	−1134	−1052	1.08	0.07	−1122	1.01	0.07	−987	1.15	0.10
	5.5	6.13	0.763	0.0187	8.45	−183	−917	−860	1.07	0.08	−929	0.99	0.08	−845	1.09	0.11
	5	5.63	0.694	0.0215	6.10	−160	−680	−667	1.02	0.11	−732	0.93	0.11	−613	1.11	0.14
	4.8	5.43	0.657	0.0228	4.88	−154	−580	−550	1.05	0.13	−607	0.96	0.13	−540	1.07	0.16
	4.6	5.24	0.611	0.0243	3.65	−139	−473	−418	1.13	0.17	−466	1.02	0.17	−433	1.09	0.20
5	11.8	12.28		0.0042		−292	−1306							−1378	0.95	0.09
	11.4	11.95		0.0055		−292	−1218							−1325	0.92	0.09
	11	11.63		0.0068		−292	−1123							−1268	0.89	0.08
	10.4	11.08		0.0092		−240	−981							−855	1.15	0.10
	10	10.69		0.0109		−218	−878							−704	1.25	0.11
	9.4	10.12		0.0138		−202	−720							−561	1.28	0.13
	9	9.71		0.0158		−202	−608							−508	1.20	0.13
	8	8.77		0.0212		−160	−305							−266	1.15	0.21
6	2.8	3.27	0.826	0.004	−2.8	2060	2366	1531	1.55	0.17	2171	1.09	0.17	2025	1.17	0.05
	3	3.49	0.763	0.004	−3.75	1760	2193	2127	1.03	0.19	3739	0.59	0.19	1792	1.22	0.06
	3.08		0.742	0.004	−4.05		2125				4429	0.48	0.21			
	3.12		0.732	0.004	−4.15		2093				4342	0.48	0.21			
	3.2	3.68	0.715	0.004	−4.6	1400	2028	2763	0.73					1522	1.33	0.06
	3.4	3.90	0.674	0.004	−5.45	1050	1875	3465	0.54					1232	1.52	0.08
	3.6	4.12	0.638	0.004	−5.80	1050	1730	2806	0.62					1189	1.46	0.07
	3.68		0.623	0.004	−6.00		1674									
	3.72		0.617	0.004	−6.00		1646				5640	0.29	0.26			
	3.8	4.34	0.604	0.004	−6.20	980	1593	2448	0.65	0.18	4855	0.33	0.18	1096	1.45	0.08
	4	4.56	0.573	0.005	−6.35	980	1462	1970	0.74	0.10	2918	0.48	0.10	1057	1.38	0.08
	4.4	4.99	0.512	0.005	−6.65	980	1221	1417	0.86	0.10	1829	0.67	0.10	978	1.25	0.08
	5	5.63	0.422	0.006	−6.65	910	892	851	1.05	0.10	1021	0.87	0.10	805	1.11	0.08
	5.4	6.04	0.362	0.006	−6.65	800	699	626	1.12	0.11	726	0.96	0.11	648	1.08	0.10
	6	6.67	0.272	0.007	−6.65	590	429	386	1.11	0.15	438	0.98	0.15	396	1.08	0.15
	6.4	7.12	0.208	0.008	−5.55	455	266	214	1.24	0.24	240	1.11	0.24	246	1.08	0.22
7	17.5	18.14	0.955	0.0042	156	−396	−3783	−2922	1.30	0.03	−2964	1.28	0.03	3094	1.22	0.16
	17	17.62	0.951	0.0055	156	−396	−3701	−2949	1.26	0.03	−2992	1.24	0.03	3022	1.22	0.16
	16	16.65	0.945	0.0080	148.5	−396	−3533	−2947	1.20	0.03	−2994	1.18	0.03	2907	1.22	0.15
	15	15.65	0.938	0.0105	138	−396	−3362	−2922	1.15	0.03	−2972	1.13	0.03	2792	1.20	0.14
	14	14.70	0.930	0.0130	118	−396	−3175	−2799	1.13	0.03	−2856	1.11	0.03	2676	1.19	0.13
	13	13.60	0.918	0.0156	83.3	−396	−2971	−2473	1.20	0.03	−2523	1.18	0.03	2535	1.17	0.12
	12	12.72	0.903	0.0182	61.0	−375	−2752	−2184	1.26	0.03	−2247	1.23	0.03	2069	1.33	0.11
	11	11.72	0.886	0.0208	47.0	−353	−2518	−1974	1.28	0.04	−2039	1.23	0.04	1716	1.47	0.11
	10	10.76	0.860	0.0238	31.2	−349	−2261	−1623	1.39	0.05	−1685	1.34	0.05	1565	1.44	0.10
	9	9.78	0.823	0.0267	24.2	−334	−1976	−1435	1.38	0.05	−1509	1.31	0.05	1319	1.50	0.10
	8	8.78	0.773	0.0297	15.75	−324	−1660	−1117	1.49	0.06	−1188	1.40	0.06	1118	1.48	0.10
	7	7.71	0.686	0.0328	8.9	−316	−1301	−741	1.76	0.09	−797	1.63	0.09	887	1.47	0.11
	6	6.83	0.543	0.0363	5.50	−273	−889	−451	1.97	0.15	−502	1.77	0.15	534	1.66	0.16
	5	6.13	0.320	0.0405	3.33	−214	−402	−187	2.15	0.35	−225	1.79	0.35	201	2.00	0.42

a)　Symbol δ represents the denominator of the ν_r expression (7), (9), (10), or (12).

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where γ is $\ln\{1+(ZD/2N)\}$.

Numerical calculations of E_ν were made by setting

$$e_A = 0.1 \text{ mmHg}$$
$$e_B = 0.1 \text{ mmHg}$$
$$e_Z = 0.01 \text{ for runs 2, 4, 6 and 7}$$
$$= 0.001 \text{ for runs 1 and 5}$$
$$e_D/D = 0.03$$
$$e_N = 2 \text{ mmHg}$$

These values are probable errors determined by inspection of Figs. 3, 4, and 5. Therefore, the E_ν values worked out using Eq. (iv) or (v) may well be called probable errors of ν_r. The results of the E_ν calculations are summarized in the Table. Run 5 lacked Z^A measurements and hence the Z_i' value needed for the error calculations. In order to enable the calculations to be made for this run, it was assumed that Z^A was 0.960 for the starting reaction mixture. This Z^A value, combined with the natural abundance of N-15 (0.00365), yielded a Z_i' value of 0.0314.

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