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## THE RATE-DETERMINING STEP OF AMMONIA SYNTHESIS AND DECOMPOSITION

### Part 2. The Effect of Ammonia Adsorption on Experimental Value for the Stoichiometric Number of the Rate-Determining Step<sup>\*)</sup>

By

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#### Abstract

A few expressions for  $\nu_r$  (the stoichiometric number of the rate-determining step) were derived by taking ammonia adsorption into account. The data in the previous paper by the author [this Journal, 13, 119 (1965)] were analyzed on the basis of these expressions. The results were compared with those obtained from the previous expressions which neglected the ammonia adsorption. In decomposition, values close to unity were obtained for  $\nu_r$  independent of which kind of expression was used. Also in synthesis, the expressions with the adsorption correction gave values close to unity for  $\nu_r$  over the ammonia pressure range studied, while the  $\nu_r$  value obtained from some expressions without the correction decreased from near unity to zero with decreasing ammonia pressure. Since the experimental conditions except ammonia pressure were identical in these experiments ammonia pressure was always greater in decomposition than in synthesis. The results above-mentioned, therefore, indicate that in lower ammonia pressures the ammonia adsorption greatly shifts the observed  $\nu_r$  value from the true one unless the correction is made to the adsorption. The results also afford additional evidence in support of our previous conclusion (loc. cit) that nitrogen chemisorption and desorption are rate-determining for ammonia synthesis and decomposition respectively over singly-promoted iron catalyst.

#### Introduction

An investigation has previously<sup>1)</sup> been made to determine the rate-determining step of catalyzed ammonia synthesis and decomposition,



The rate-determining step was determined by finding out directly such steps

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that are in partial equilibrium as well as by measuring  $\nu_r$ , the stoichiometric number of the rate-determining step. The finding of partially equilibrated steps and the measurement of  $\nu_r$  were conducted simultaneously in a single run by using nitrogen-15 as tracer. The intermediate, chemisorbed nitrogen, was found to be in partial equilibrium with gaseous ammonia, but not with gaseous nitrogen, in the courses of both ammonia synthesis and decomposition. This indicates that nitrogen chemisorption and desorption steps are rate-determining for ammonia synthesis and decomposition respectively. In order to evaluate  $\nu_r$  with the same experimental data, three expressions (*cf.* Table 1 of this paper) were derived by ignoring ammonia adsorption, which was actually detected on the catalyst surface and glass walls. In decomposition, any of these three gave values close to unity for  $\nu_r$ . This coincides with the above mentioned indication that nitrogen desorption is rate-determining. Also in synthesis, the values for  $\nu_r$  evaluated from one of these expressions were close to unity over the ammonia pressure range studied. However, the values evaluated from the other two decreased from near unity to zero with decreasing ammonia pressure, and as the pressure further decreased the values became meaningless, the argument of the logarithmic function in these expressions becoming negative. Our previous paper<sup>1)</sup> noticed that this anomaly might be explained as resulting from the observed ammonia adsorption.

The present work is therefore aimed at deriving expressions for  $\nu_r$  without ignoring the ammonia adsorption and at re-analyzing the previous data by these expressions.

### 1. Expressions for $\nu_r$

In order to derive expressions for  $\nu_r$  taking the ammonia adsorption into account, let us consider a mixture of hydrogen, nitrogen and ammonia which is in contact with ammonia synthesis catalyst. Either the nitrogen or ammonia is labeled with  $N^{15}$ . A fraction of the ammonia is adsorbed on the catalyst surface and apparatus walls. The partial pressures of each gas and the transfer of  $N^{15}$ -atoms from nitrogen to ammonia or the reverse are followed at a constant total pressure until ammonia synthesis or decomposition attains equilibrium. For simplicity we shall restrict our consideration to a case in which the adsorbed ammonia is in partial equilibrium with gaseous ammonia but not with gaseous nitrogen. Furthermore, the amount adsorbed is assumed to be independent of ammonia pressure, and therefore to be kept constant throughout the course of the reaction. It is to be noted that these conditions were closely realized in our previous experiments whose data are re-analyzed in this paper.

In the presence of a rate-determining step we have the general relation

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$$\nu_r = \frac{-\Delta F}{RT \ln(V_+/V_-)}, \quad (2)$$

where  $-\Delta F$  is the chemical affinity associated with 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. 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

$$-\Delta F = RT \ln(P_H^3 P_N K_s / P_A^2). \quad (3)$$

The net rate  $V$  may be written as

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

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. Since  $da_{(a)}/dt$  is equal to zero according to the premise previously mentioned, the above equation reduces to

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

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

The rate of  $N^{15}$ -transfer from nitrogen to ammonia or the reverse may be expressed as

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

or

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

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,  $(N^{14}N^{15} + 2N^{15}N^{15})/2(N^{14}N^{14} + N^{14}N^{15} + N^{15}N^{15})$ , respectively. Combining Eqs. (5. a) and (6. a) we find

$$\frac{V_+}{V_-} = \frac{\{(a + a_{(a)})/2(Z^N - Z^A)\} dZ^A/dt}{\{(a + a_{(a)})/2(Z^N - Z^A)\} dZ^A/dt - (1/2) da/dt} \quad (7. a)$$

$$= \frac{1}{1 - \{(Z^N - Z^A)/(a + a_{(a)})\} da/dZ^A}. \quad (7. b)$$

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Assuming ideal gas behavior for ammonia, this equation may be rewritten as

$$\frac{V_+}{V_-} = \frac{1}{1 - \{(Z^N - Z^A)/(P_A + a_{(a)}RT/V_i)\} dP_A/dZ^A}, \quad (7. c)$$

where  $V_i$  is the volume of the reaction system. Substituting  $-dF$  and  $V_+/V_-$  respectively from Eqs. (3) and (7.c) into (2) we finally get, as an expression for  $\nu_r$ ,

$$\nu_r = \frac{RT \ln (P_H^3 P_N K_s / P_A^2)}{RT \ln \left[ 1 / \left\{ 1 - \frac{Z^N - Z^A}{P_A + a_{(a)} RT / V_i} \left( \frac{dP_A}{dZ^A} \right) \right\} \right]}. \quad (8)$$

On the other hand, solving Eqs. (5.b) and (6.b) for  $V_+$  and  $V_-$ , remembering that  $dn/dt = -(1/2)da/dt$ , and assuming ideal gas behavior for both nitrogen and ammonia, we find

$$\frac{V_+}{V_-} = \frac{\{ndZ^N/(Z^A - Z^N)dt\} + (1/2)da/dt}{ndZ^N/(Z^A - Z^N)dt} \quad (9. a)$$

$$= 1 + (P_A/2P_N)(Z^A - Z^N)d \ln P_A/dZ^N. \quad (9. b)$$

Another expression for  $\nu_r$  is thus given by

$$\nu_r = \frac{RT \ln (P_H^3 P_N K_s / P_A^2)}{RT \ln \{1 + (P_A/2P_N)(Z^A - Z^N)d \ln P_A/dZ^N\}}. \quad (10)$$

At any time during the course of the reaction we have

$$Z^A(a + a_{(a)}) + 2Z^N n = Z'_i(a + a_{(a)} + 2n) \quad (11. a)$$

or in terms of pressure

$$Z^A(P_A + a_{(a)}RT/V_i) + 2Z^N P_N = Z'_i(P_A + 2P_N + a_{(a)}RT/V_i), \quad (11. b)$$

where  $Z'_i$  is the value of  $Z^A$  and  $Z^N$  at the exchange equilibrium of  $N^{15}$ -atoms among gaseous ammonia, gaseous nitrogen and adsorbed ammonia. Elimination of  $Z^N$  from Eq. (8) by the use of Eq. (11.b) yields

$$\nu_r = \frac{RT \ln (P_H^3 P_N K_s / P_A^2)}{RT \ln \left[ 1 / \left\{ 1 - \left( 1 + \frac{P_A + a_{(a)}RT/V_i}{2P_N} \right) \left( \frac{Z'_i - Z^A}{P_A + a_{(a)}RT/V_i} \right) \left( \frac{dP_A}{dZ^A} \right) \right\} \right]}. \quad (12)$$

In Table 1, the three expressions for  $\nu_r$  derived in this paper are listed, and compared with those derived in our previous paper<sup>1)</sup> by ignoring the ammonia adsorption. Eqs. (8) and (12) of this paper, which involve the derivative  $dP_A/dZ^A$ , reduce respectively to those of our previous paper only in case  $a_{(a)}$

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TABLE 1. Comparison between several expressions for  $\nu_r$

Expressions for $\nu_r$	Remarks
$- \Delta F/RT \ln \left[ 1 / \left\{ 1 - \frac{Z^N - Z^A}{P_A + a_{(a)} RT/V_i} \left( \frac{dP_A}{dZ^A} \right) \right\} \right]$	(8) derived in this paper taking ammonia adsorption into account.
$- \Delta F/RT \ln \left\{ 1 + (P_A/2P_N)(Z^A - Z^N) d \ln P_A/dZ^N \right\}$	(10) ignoring ammonia adsorption
$- \Delta F/RT \ln \left[ 1 / \left\{ 1 - \left( 1 + \frac{P_A + a_{(a)} RT/V_i}{2P_N} \right) \left( \frac{Z'_i - Z^A}{P_A + a_{(a)} RT/V_i} \right) \left( \frac{dP_A}{dZ^A} \right) \right\} \right]$	(12) derived in previous paper
$- \Delta F/RT \ln \left[ 1 / \left\{ 1 - (Z^N - Z^A) d \ln P_A/dZ^A \right\} \right]$	(8) ignoring ammonia adsorption
$- \Delta F/RT \ln \left\{ 1 + (P_A/2P_N)(Z^A - Z^N) d \ln P_A/dZ^N \right\}$	(10) ignoring ammonia adsorption
$- \Delta F/RT \ln \left[ 1 / \left\{ 1 - \left( 1 + \frac{P_A}{2P_N} \right) (Z'_i - Z^A) \left( \frac{d \ln P_A}{dZ^A} \right) \right\} \right]$	(12) ignoring ammonia adsorption

declines to zero<sup>\*)</sup>, whereas Eqs. (10) of this and previous papers, which involve the derivative  $d \ln P_A/dZ^N$  in place of  $dP_A/dZ^A$ , are of the same form independent of  $a_{(a)}$ . In this connection it should be remembered that in our previous work the  $\nu_r$  values obtained by Eq. (10) were close to unity, independent of  $P_A$ , while the  $\nu_r$  values obtained from Eq. (8) or (12) were anomalous in a lower  $P_A$  region as was described in Introduction.

## 2. Analysis of Our Previous Data

The experimental data of our previous work are now analyzed by Eq. (8) or (12) derived in this paper, and the results are compared with those obtained by ignoring ammonia adsorption. In each run of the work, the adsorption of ammonia apparently occurred on both the catalyst surface and glass walls of the apparatus. In addition to this adsorbed ammonia there was residual nitrogen on the catalyst. The residual nitrogen refers to the nitrogen or nitrogen-containing species which was left on the catalyst after evacuating it for three hours at 400°C between runs. The amounts of these adsorbed ammonia and residual nitrogen are listed in Table 2. They were all in partial equilibrium with gaseous ammonia, although their actual form on the catalyst surface is still unknown. The  $a_G$  and  $n_R$  were constant independent of ammonia pressure, while  $a_C$  increased with increasing ammonia pressure<sup>\*\*)</sup>. The sum

\*) In our previous paper,  $Z'_i$  was defined as the value of  $Z^A$  or  $Z^N$  at the exchange equilibrium of  $N^{15}$ -atoms between gaseous ammonia and gaseous nitrogen. The  $Z'_i$  in this paper, therefore, becomes identical with this  $Z'_i$  when  $a_{(a)}$  is zero.

\*\*\*) The  $a_C$  value in Table 2 was taken as the average value over the course of each run.

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TABLE 2. The amounts of adsorbed ammonia and residual nitrogen in each run of our previous work.

Run	$a_G$ ( $\mu$ mole)	$a_C$ ( $\mu$ mole)	$n_R$ ( $\mu$ mole)	$a_S$ ( $\mu$ mole)
3	37	35	51	123
4	"	50	"	138
5	"	45	"	133
6	"	60	"	148

$a_G$ ,  $a_C$ , and  $n_R$  are the amounts of ammonia adsorbed on the glass walls, ammonia adsorbed on the catalyst, and the residual nitrogen left on the catalyst respectively.  $a_S$  is the sum of  $a_G$ ,  $a_C$  and  $n_R$ .

of  $a_G$ ,  $a_C$  and  $n_R$ , designated as  $a_S$ , however, can be regarded as approximately constant in the course of a run because the variation in  $a_C$  was less than  $20 \mu$  moles in a run while  $a_S$  was more than  $120 \mu$  moles as is seen in Table 2. The  $a_{(a)}$  in Eqs. (8) and (12) may, therefore, be approximated by  $a_S$ .

Kinetic data necessary for evaluating  $\nu_s$  are also reproduced in Tables 3 a-d. The values for  $Z^A$ ,  $Z^N$  and  $P_A$  except those at  $t=\infty$  and  $Z^N$  at  $t=0$  were measured directly by a mass spectrometer or manometer. The  $Z^N$  value at  $t=0$  was assumed to be 0.00365, the natural abundance of  $N^{15}$ . For runs 4 to 6, the value for  $Z'_i$ , *i.e.* the value for  $Z^A$  or  $Z^N$  at  $t=\infty$ , has previously

TABLE 3a. Kinetic data of run 3 of our previous work. Ammonia synthesis at  $340^\circ\text{C}$ .

Sample	$t$ (h)	$Z^A$	$P_A$ (mm Hg)	$V_i$ ( $\ell$ )	$a_{(a)}RT/V_i$ (mm Hg)	$P_A + \frac{a_{(a)}RT}{V_i}$ (mm Hg)	$Z^N$
0	0	0.961	1.96	2.258	1.01	2.97	0.00365
1	0.3	0.816	1.73	2.072	1.10	2.74~2.83	
2	5.0	0.723	2.26	1.864	1.22	3.36~3.48	
3	13.8	0.567	2.68	1.766	1.29	3.90~3.97	
4	24.8	0.461	3.00	1.669	1.36	4.29~4.36	
5	37.8	0.360	3.32	1.578	1.44	4.68~4.76	
6	57.8	0.266	3.59	1.486	1.53	5.03~5.12	
7	77.8	0.194	3.67	1.386	1.64	5.20~5.31	
8	101.8	0.126	3.78	1.288	1.76	5.42~5.54	
9	123.8	0.129	3.80			5.56	
	$\infty$	0.012 (= $Z'_i$ )	3.8				0.012 (= $Z'_i$ )

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TABLE 3 b. Kinetic data of run 4 of our previous work.  
Ammonia decomposition at 340°C.

Sample	$t$ (h)	$Z^A$	$P_A$ (mm Hg)	$V_i$ (ℓ)	$\frac{a_{(a)}RT}{V_i}$ (mm Hg)	$P_A + \frac{a_{(a)}RT}{V_i}$ (mm Hg)	$Z^N$
0	0	0.951	7.97	2.257	1.13	9.10	0.00365
1	0.5	0.905	7.45	2.160	1.18	8.58~8.63	
2	3.0	0.890	7.19	2.071	1.23	8.37~8.42	0.0049
3	10.0	0.836	6.23	1.975	1.29	7.46~7.52	0.0106
4	19.0	0.745	5.34	1.878	1.36	6.63~6.70	
5	26.0	0.658	4.72	1.792	1.42	6.03~6.14	
6	35.0	0.554	4.25	1.698	1.50	5.67~5.75	0.0226
7	47.0	0.416	4.15	1.599	1.59	5.65~5.74	
8	59.0	0.300	4.04	1.507	1.69	5.63~5.73	0.0282
9	80.0	0.166	3.97	1.410	1.81	5.66~5.78	0.0301
10	105.0	0.084	3.96	1.318	1.93	5.77~5.89	0.0329
11	128.0	0.033	3.76			5.69	0.0332
	∞	0.033 (= $Z_i^0$ )	3.8				0.033 (= $Z_i^0$ )

TABLE 3 c. Kinetic data of run 5 of our previous work.  
Ammonia synthesis at 305°C.

Sample	$t$ (h)	$Z^A$	$P_A$ (mm Hg)	$V_i$ (ℓ)	$\frac{a_{(a)}RT}{V_i}$ (mm Hg)	$P_A + \frac{a_{(a)}RT}{V_i}$ (mm Hg)	$Z^N$
0	0	0.930	3.71	2.242	1.10	4.81	0.00365
1	0.5	0.851	3.39	2.144	1.15	4.49~4.54	
2	5.0	0.822	3.46	2.052	1.20	4.61~4.66	0.0039
3	21.0	0.755	3.77	1.952	1.26	4.97~5.03	
4	36.0	0.709	3.83	1.862	1.32	5.09~5.15	0.0046
5	57.0	0.625	4.57	1.761	1.40	5.89~5.97	0.0057
6	82.0	0.580	4.78	1.662	1.48	6.18~6.26	
7	115.0	0.507	5.22	1.563	1.57	6.70~6.79	0.0065
8	160.0	0.441	5.69	1.474	1.67	7.26~7.36	
9	203.0	0.358	5.96	1.370	1.80	7.63~7.76	
10	251.0	0.323	6.29	1.273	1.93	8.09~8.22	0.0099
11	302.1	0.273	6.53			8.46	
	∞	0.019 (= $Z_i^0$ )	7.0				0.019 (= $Z_i^0$ )

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 TABLE 3 d. Kinetic data of run 6 of our previous work.  
 Ammonia decomposition at 305°C.

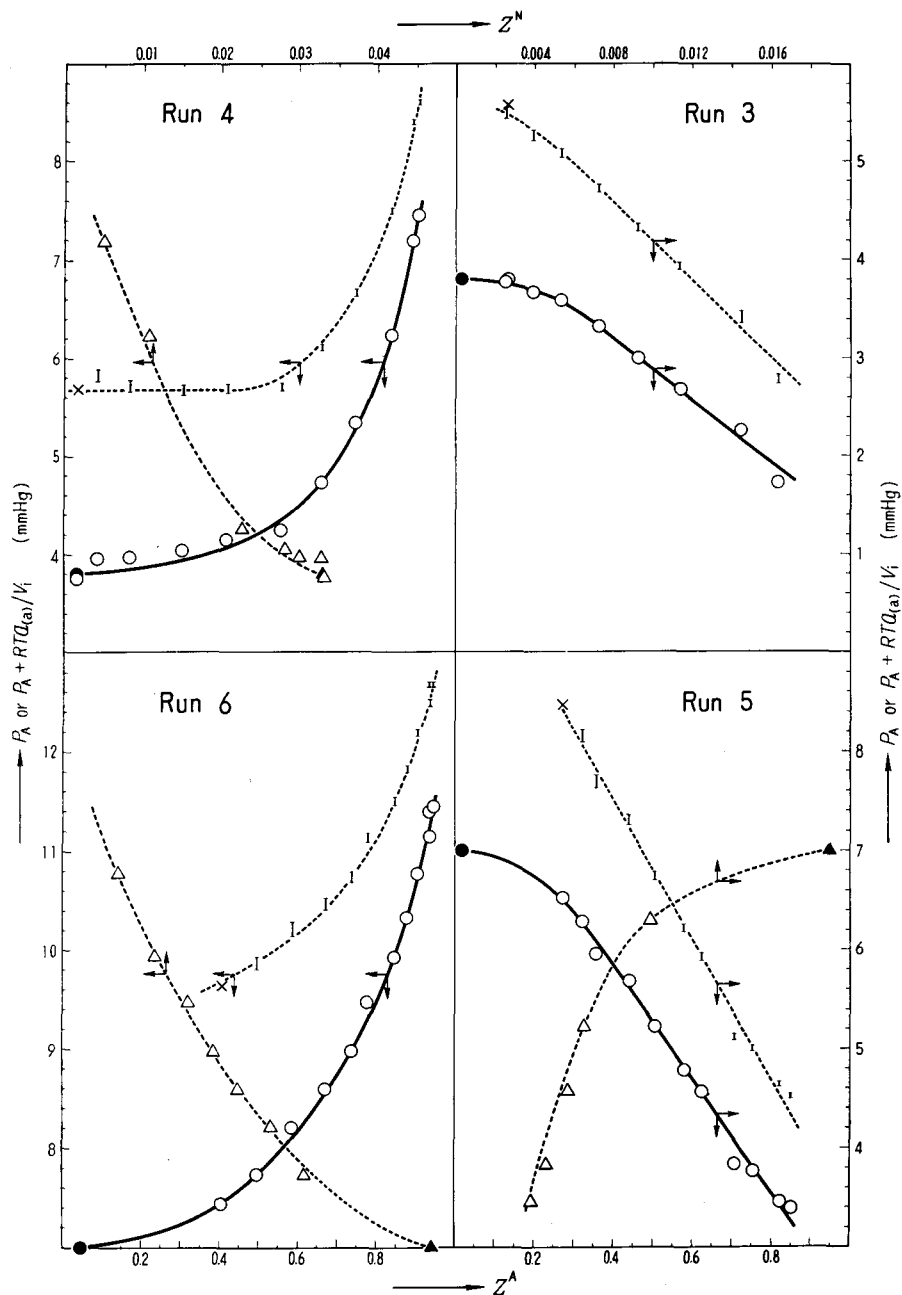
Sample	$t$ (h)	$Z^A$	$P_A$ (mm Hg)	$V_t$ ( $\ell$ )	$\frac{a_{(a)}RT}{V_t}$ (mm Hg)	$P_A + \frac{a_{(a)}RT}{V_t}$ (mm Hg)	$Z^N$
0	0	0.976	11.89	2.258	1.21	13.10	0.00365
1	0.5	0.944	11.44	2.168	1.26	12.65~12.70	
2	5.0	0.933	11.39	2.079	1.31	12.65~12.70	
3	22.0	0.936	11.14	1.984	1.38	12.45~12.52	
4	48.0	0.905	10.77	1.885	1.45	12.15~12.22	0.0070
5	78.0	0.879	10.33	1.792	1.52	11.78~11.85	
6	116.0	0.847	9.93	1.697	1.61	11.45~11.54	0.0116
7	163.0	0.778	9.47	1.607	1.70	11.08~11.17	0.0159
8	211.0	0.738	8.98	1.508	1.81	10.68~10.79	0.0192
9	267.0	0.672	8.59	1.411	1.93	10.40~10.52	0.0224
10	338.0	0.587	8.21	1.320	2.07	10.14~10.28	0.0265
11	428.0	0.496	7.73	1.239	2.20	9.80~9.93	0.0308
12	528.0	0.405	7.44			9.64	
	$\infty$	0.047 (= $Z'_i$ )	7.0				0.047 (= $Z'_i$ )

been calculated<sup>1)</sup>. For run 3, the  $Z'_i$  was calculated from Eq. (11. b) by using the data at  $t=0$  and remembering that the total pressure is 550 mmHg and  $P_H : P_N = 3 : 1$ . The volume of the reaction system designated as  $V_t$  was practically constant between samplings. The  $a_{(a)}RT/V_t$  values were calculated by approximating  $a_{(a)}$  by  $a_x$  and putting  $T$  to 296°K, the room temperature during the reaction.

In Fig. 1,  $P_A$  and  $P_A + a_{(a)}RT/V_t$  are plotted against  $Z^A$  for each run, besides a  $P_A$  versus  $Z^N$  plot is given for runs 4 to 6. These data were used to calculate  $\nu_r$  allowing the ammonia adsorption. In the case of run 3, the calculation was made with Eq. (12) for several values of  $P_A$  by reading the relevant  $Z^A$  and  $P_A + a_{(a)}RT/V_t$  values and estimating the slope of  $P_A$  versus  $Z^A$  plot and further by evaluating  $P_H$  and  $P_N$  from  $P_H = \frac{3}{4}(550 - P_A)$  and  $P_N = \frac{1}{4}(550 - P_A)$  mmHg. In the case of runs 4 to 6, the calculation was made in a similar manner by using Eq. (8). As will be discussed in Appendix, this procedure for calculating  $\nu_r$  is not justifiable unless  $a_{(a)}$  is zero, but gives an approximate  $\nu_r$  value even if  $a_{(a)}$  is not zero.

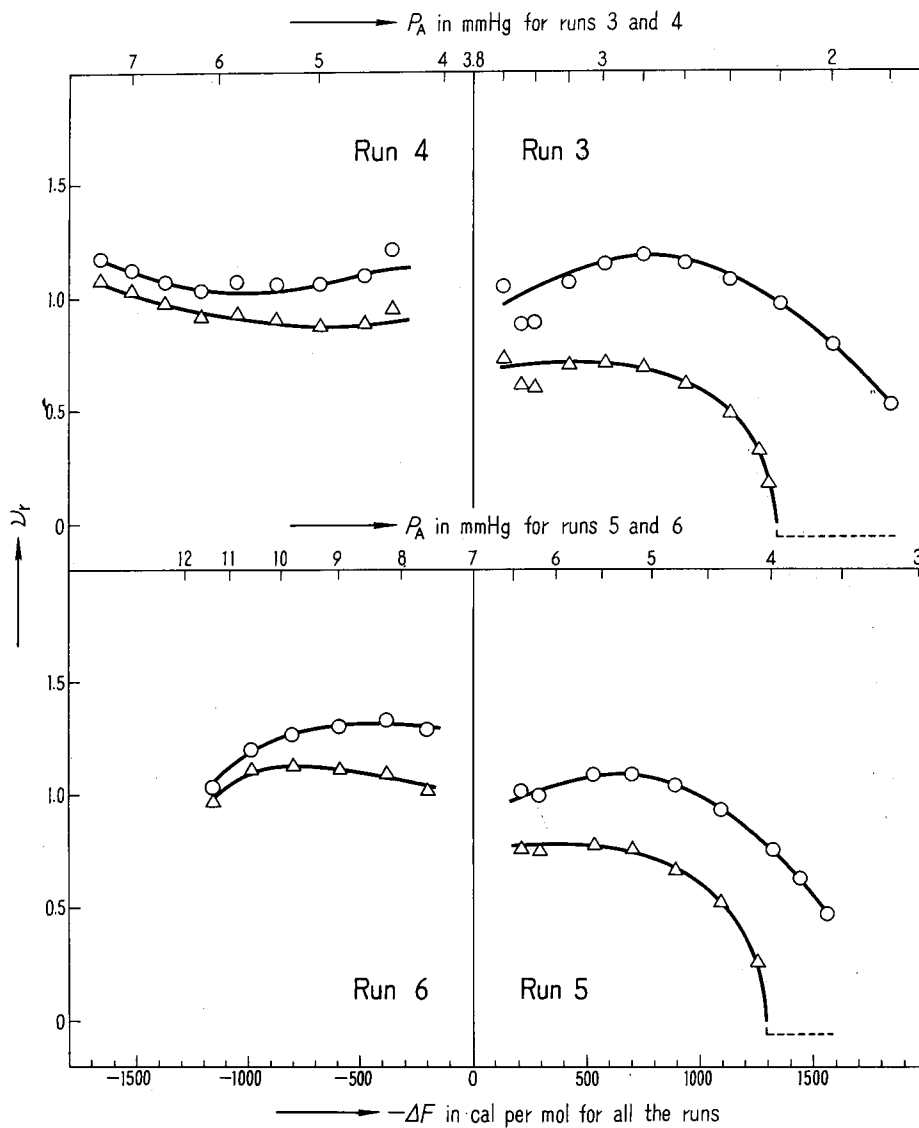
As is seen in Table 1, the expressions (8) and (12) derived in our previous paper involve the derivative  $d \ln P_A / dZ^A$ . By remembering that this is equivalent with  $(1/P_A) dP_A / dZ^A$ , the  $\nu_r$  value without the adsorption correction can also be evaluated by the use of the  $P_A$  versus  $Z^A$  curve in Fig. 1 in a similar

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**Fig. 1.** Graphic presentation of the data in Tables 3a-d. The value for  $Z_i$  at  $t = \infty$  is shown by solid circle and solid triangle.

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**Fig. 2.** The effect of ammonia adsorption on experimental value for  $\nu_r$ .

○ is the  $\nu_r$  value with the adsorption correction and △ is that without it. Broken lines show the  $-\Delta F$  region where the latter  $\nu_r$  value is meaningless as the argument of the logarithmic function in the expressions for  $\nu_r$  is negative.

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way to in the above case of the  $r_r$  value with the correction.

In Fig. 2, the  $\nu_r$  values thus calculated with the adsorption correction are contrasted with those thus calculated without the correction<sup>\*)</sup>. In synthesis, the latter  $\nu_r$  value decreases with increasing chemical affinity to zero, and as the affinity further increases, the  $\nu_r$  becomes meaningless, the argument of the logarithmic function in Eqs. (8) and (12) without the correction becoming negative, whereas the former  $\nu_r$  value is close to unity except a region where chemical affinity is very high. In decomposition, the  $\nu_r$  is close to unity whether the adsorption is considered or not. These results seem to suggest that the true value for  $\nu_r$ , not masked by ammonia adsorption, is just unity over the ammonia pressure range studied and the effect of the adsorption becomes more pronounced as ammonia pressure decreases. This confirms our previous conclusion that nitrogen chemisorption and desorption is rate-determining for ammonia synthesis and decomposition respectively.

### Appendix

A procedure for evaluating the  $\nu_r$  value with the adsorption correction was given in Section 2. It will be shown that this procedure is not justified in the strict sense, but approximately right in the treatment of the data with which this paper has been concerned. Since the left side of Eq. (7. c) is the ratio of the forward unidirectional rate to the backward one, it must change continuously with time unless the atmosphere around the catalyst suddenly changes. In the experiment with which we are now concerned, every time a sample of the reaction gas was drawn from the reaction system, the volume of the system was reduced so as to keep the total pressure unchanged. No sudden change, therefore, occurred in the atmosphere in the course of this experiment, but the volume of the reaction system, which corresponds to  $V_i$  in Eq. (7. c), decreased stepwise. It may be seen, on the other hand, that  $Z^A$ ,  $Z^N$  and  $P_A$  change continuously with time. Then the derivative  $dP_A/dZ^A$  in the right side of the same equation must be discontinuous at the points corresponding to the sampling so as to make the right side itself continuous compensating for the discontinuity in  $a_{(a)}RT/V_i$ . The  $P_A$  versus  $Z^A$  curve drawn smoothly in Fig. 1, therefore, does not represent the actual  $P_A$  versus  $Z^A$  profile exactly.

\*) In our previous work<sup>1)</sup>, the  $\nu_r$  values without the correction were evaluated by the use of a  $\log P_A$  versus  $Z^A$  curve instead of a  $P_A$  versus  $Z^A$  one. The values thus calculated, however, were not reproduced in Fig. 2; for a comparison between the  $\nu_r$  values with and without the correction is preferably made by analyzing the same  $P_A$  versus  $Z^A$  plot.

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The extent of the deviation of the drawn  $P_A$  versus  $Z^A$  curve from the actual  $P_A$  versus  $Z^A$  profile is now estimated. The overall reaction rate is given by Eq. (5. a), which can be rewritten on the assumption of ideal gas behavior for ammonia as

$$V = \frac{1}{2} \frac{V_i}{RT} \frac{dP_A}{dt} \quad (i)$$

The unidirectional forward rate  $V_+$ , on the other hand, is given as the numerator of Eq. (7. a),

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

This equation can also be rewritten in terms of pressure as

$$V_+ = \frac{V_i}{RT} \left\{ \frac{P_A + a_{(a)}RT/V_i}{2(Z^N - Z^A)} \right\} \frac{dZ^A}{dt} \quad (ii)$$

Combining Eqs. (i) and (ii) yields

$$\frac{dP_A}{dZ^A} = \frac{VP_A}{V_+(Z^N - Z^A)} \left( 1 + \frac{a_{(a)}RT}{P_A V_i} \right) \quad (iii)$$

By the last equation we can assess the effect of  $V_i$  on  $dP_A/dZ^A$ . In run 3, the factor to  $1/V_i$ ,  $a_{(a)}RT/P_A$ , was calculated to range from 1.2  $\ell$  at the beginning of the reaction to 0.6  $\ell$  at the end of the reaction, while  $V_i$  decreased stepwise from 2.3 to 1.3  $\ell$  by only 0.1 or 0.2  $\ell$  for a single sampling as seen from Table 3. Therefore, the factor,  $1 + a_{(a)}RT/V_i P_A$ , is altered by only several percent by the stepped decrease in  $V_i$  due to a single sampling, and so is the derivative  $dP_A/dZ^A$ . This value is even lower in the other runs. Thus it is seen that the procedure for evaluating the  $\nu_r$  value with the adsorption correction is approximately right although it is not justified in the strict sense unless  $a_{(a)}$  is zero.

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#### Reference

- 1) K. TANAKA, This Journal, 13, 119 (1965).