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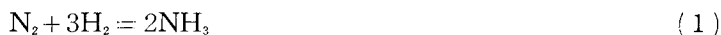
By

Juro HORIUTI and Nobutsune TAKEZAWA<sup>\*)</sup>

(Received October 7, 1960)

## Introduction

HORIUTI and TOYOSHIMA<sup>1)2)</sup> concluded from the kinetic analysis of the catalyzed decomposition of ammonia that the rate-determining step of the catalyzed synthesis of ammonia



was the third one, *i. e.* (2. I) of the sequence of the steps



on the basis of the previous result of ENOMOTO, HORIUTI and KOBAYASHI<sup>3) 4)</sup> that the stoichiometric number of the rate-determining step was two.

The prevailing view is, however, that the rate-determining step is (2.N), *i. e.* the step of the stoichiometric number one. One of the grounds of this view is the kinetic equation<sup>5)-8)</sup> of the synthesis (1) or its reversal derived from the assumed rate-determining step, which is taken to agree with the experimental results, although, as a matter of fact, not very satisfactorily<sup>9)10)</sup>.

The present paper is concerned with an experimental investigation of the kinetics of synthesis (1) for deciding between the two contrasting views<sup>\*\*)</sup>.

Let  $\bar{V}$  and  $\bar{V}$  be the unidirectional forward and backward rates of the

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<sup>\*\*)</sup> TOYOSHIMA and HORIUTI [this Journal, **6**, 146 (1958)] advanced a slight modification of the sequence (2) of the steps in accord with the result of their analysis of the hysteresis of the decomposition rate of ammonia. This modification matters, however, little to the present argument.

overall reaction at the steady state. The ratio of  $\bar{V}$  to  $\bar{V}$  is given, if there exists a rate-determining step  $r$ , as<sup>11)</sup>

$$\bar{V}/\bar{V} = (a^R/a^L K)^{1/\nu(r)}, \quad (3)$$

where  $a^L$  is the activity product of the left-hand side of the chemical equation, *e.g.* (1), of the overall reaction,  $a^R$  that of the right-hand side,  $K$  the equilibrium constant or  $a^R/a^L$  at the equilibrium and  $\nu(r)$  the stoichiometric number of the rate-determining step; the  $\nu(r)$  is 1 or 2 according as the rate-determining step of the overall reaction (1) is (2.N) or (2.I) respectively.

The directly observed rate  $V$  of the overall reaction is the excess of  $\bar{V}$  over  $\bar{V}$ , *i.e.*

$$V = \bar{V} - \bar{V} = \bar{V} \{1 - (a^R/a^L K)^{1/\nu(r)}\}, \quad (4)$$

where the factor  $1 - (a^R/a^L K)^{1/\nu(r)}$  is definite for a definite value of  $\nu(r)$  at a given experimental condition. The other factor  $\bar{V}$  of the last member of (4) is in general a function of the partial pressures of nitrogen, hydrogen and ammonia. However, those of nitrogen and hydrogen may be taken practically constant respectively in the synthesis of ammonia from 1:3 nitrogen-hydrogen mixture under 1 atm. total pressure at temperatures from 300°C to 500°C, where the partial pressure of ammonia amounts only to an exceedingly low value. The  $\bar{V}$  is in consequence practically a function solely of the partial pressure of ammonia under the specified condition.

HORIUTI and TOYOSHIMA have concluded<sup>12)</sup> that  $\bar{V}$  is proportional to the partial pressure of ammonia besides depending on that of nitrogen. This conclusion incorporated with that  $\nu(r)=2$  leads necessarily to a definite rate law  $V$  at the specified condition irrespective of the dependence of  $\bar{V}$  on the partial pressure of nitrogen according to (3) and (4). The function  $\bar{V}$  or  $\bar{V}$  proposed by other authors and the rate-determining step implied lead respectively to definite but different rate laws.

The rate of formation of ammonia was thus observed at the specified condition and by means of the results obtained, these rate laws were examined for their validity to decide the question as described in what follows.

## § 1 Materials

Catalyst used was a different portion of the same preparation as that used in the previous experiments<sup>13)</sup>, which contained 1.82% aluminium oxide, 1.06% potassium oxide, 0.41% silica, 0.04% calcium oxide and a trace of magnesium oxide.<sup>1)</sup> The catalyst was reduced with cylinder hydrogen purified by passing it successively over reduced copper and nickel gauzes, respectively of 39 and

31 cm<sup>3</sup> apparent volumes and kept both at 600°C, through four columns of silica gel and then over phosphorus pentoxide.

The gas mixture of 1 : 3 nitrogen-hydrogen was prepared by decomposing cylinder ammonia dried over soda lime and solid potassium hydroxide, over the synthetic catalyst kept at 600–700°C and passed through a purification train, which consisted of a wash bottle of conc. sulfuric acid solution, a column of

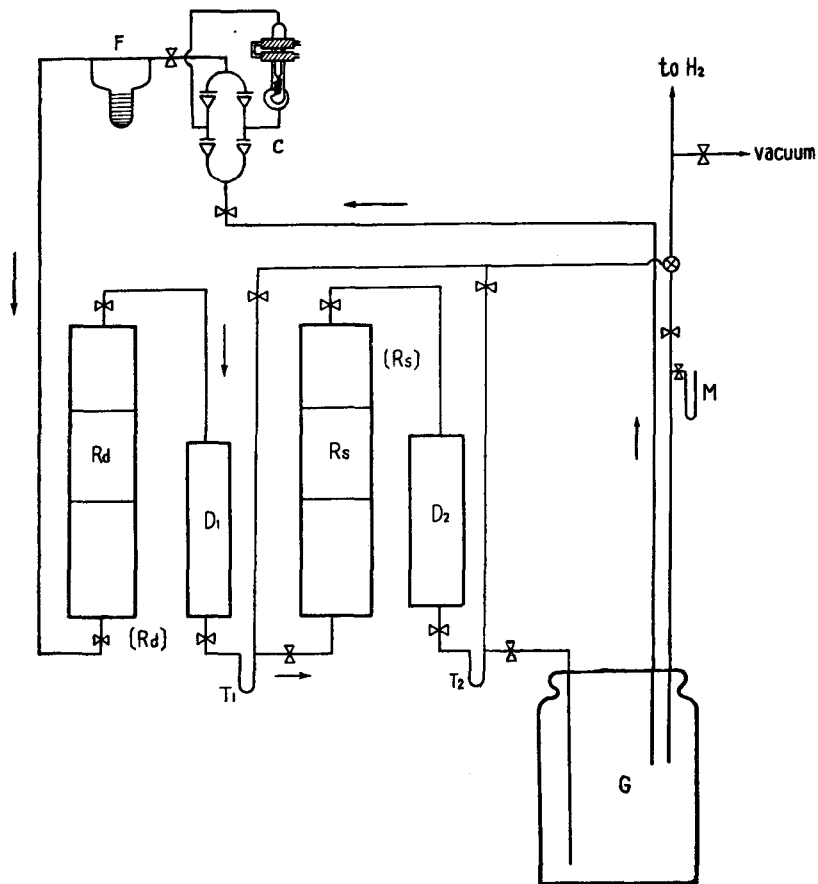


Fig. 1. Apparatus for reduction of catalysts.

- C : Circulation pump
- D<sub>1</sub>, D<sub>2</sub> : Drying agents (silica gel)
- F : Flow meter
- G : Gas holder
- M : Manometer
- [R<sub>d</sub>] : Reaction chamber packed with the catalyst R<sub>d</sub> for decomposition
- [R<sub>s</sub>] : Reaction chamber packed with the catalyst R<sub>s</sub> for synthesis
- T<sub>1</sub>, T<sub>2</sub> : Traps immersed in liq. nitrogen

solid sodium hydroxide, a trap immersed in liquid nitrogen, a converter of 42 g copper gauze kept at 600°C, that of 11 g nickel gauze kept at the same temperature and two columns of silica gel, for removing undecomposed ammonia, carbon dioxide, moisture, oxygen and carbon monoxide.

## § 2 Reduction of catalyst

Fig. 1 illustrates schematically a separate apparatus for reducing the catalyst  $R_d$  for decomposition of ammonia mentioned and the catalyst  $R_s$  for the synthesis experiment in question, which are respectively of 105 and 88.5 g weights and 69 and 48.2 cc apparent volumes before reduction, each packed in the quartz reaction chamber  $[R_d]$  or  $[R_s]$  provided with two taps at its both ends. These catalysts are reduced simultaneously by circulating hydrogen purified as described in § 1, by means of the circulation pump  $C$  in the direction of arrows, at the 1500 cc/min flow rate first for 202 hours at 300°C, now for 260 hours at 350°C, then for 173 hours at 400°C and finally for 571 hours at 550°C. Water formed by reduction is removed by the columns  $D_1$  and  $D_2$  of silica gel and the traps  $T_1$  and  $T_2$  immersed in liquid nitrogen. The progress of reduction is followed roughly by the decrease of hydrogen pressure on the manometer  $M$ . The reduction is continued until the fresh condensation overnight of water in the preliminarily cleaned trap\*)  $T_1$  or  $T_2$  is imperceptible. The reaction chambers  $[R_d]$  and  $[R_s]$  are now closed up each by the taps attached and removed from this apparatus to be built in that for the experiment.

## § 3 Apparatus for synthesis

The apparatus for the synthesis experiment is shown in Fig. 2. The reaction chamber  $[R_s]$ , in which the catalyst bed  $R_s$  is packed and reduced as described in § 2, is of 1 m length and 3.5 cm inner diameter; quartz wool, porcelain Raschig rings and quartz fragments of 8–10 mesh are packed above and below  $R_s$  as shown in Fig. 2 in order to support it, to preheat the gas mixture entering the catalyst bed and to keep the temperature inside homogeneous. The quartz reaction chamber  $[R_d]$  is similarly packed but without the quartz fragments. The temperature of the catalyst bed is measured by alumel-chromel thermojunctions  $J_1$  and  $J_2$ , calibrated at the melting points of tin, lead, zinc, cadmium and antimony. The thermojunctions  $J_1$  and  $J_2$  slide each through a quartz blind tube of 2 mm external diameter fitted, as shown in Fig. 2, just inside the wall or along the axis respectively of the reaction

\*) The trap is cleaned by closing it to the catalysts and opening to the vacuum by a proper manipulation of taps.

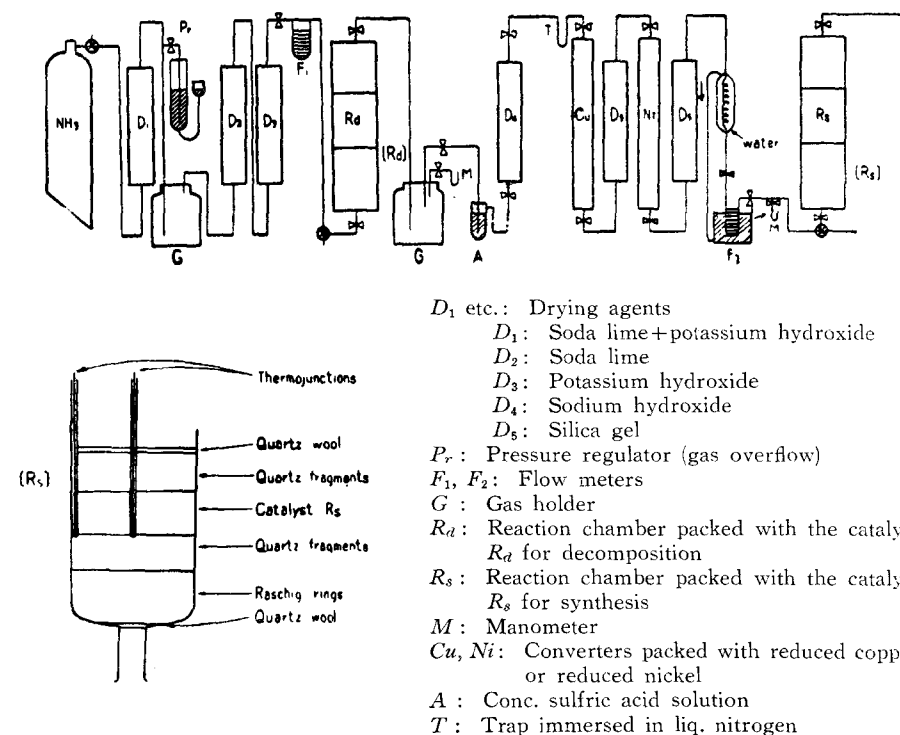


Fig. 2. Apparatus for ammonia synthesis experiments.

chamber. The  $J_1$  is automatically kept at the desired temperature by means of a potentiometric thermoregulator within  $\pm 2^\circ\text{C}$  except when otherwise remarked.  $P_r$  is the gas overflow for keeping the gas pressure constant at 1 atm. pressure in the apparatus.  $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$  and  $D_5$  are the towers of drying agents.  $F_1$  and  $F_2$  are flowmeters for measuring the flow rates of ammonia and of gas mixture respectively. The temperature of  $F_2$  is kept constant at  $12^\circ\text{C}$  in a bath of tap water. The wash bottle  $A$  contains conc. sulfuric acid solution for removing undecomposed ammonia from the gas mixture.

#### § 4 Procedure of experiment

The 1 : 3 nitrogen-hydrogen gas mixture was allowed to flow at a constant flow rate through  $R_s$  at a constant temperature until a steady synthesis of ammonia was attained in each run conducted in series. The series was begun by raising the temperature of the catalyst bed  $R_s$  to that of first run of the series under the constant inflow rate of nitrogen-hydrogen mixture. Two hours after the temperature was attained, the outflow rate  $N_d$  of ammonia was begun to be

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measured repeatedly, until it attained a constant value. One to three runs were conducted usually per day switching from one to the other constant flow rate or temperature. On closing the daily work,  $R_s$  was allowed to cool in the nitrogen-hydrogen mixture down to room temperature and kept in the gas mixture overnight. The daily work was initiated just as in the beginning of the series.

The  $N_A$  was determined by passing the gas mixture through sulfuric acid solution of known concentration and quantity for a recorded time and by titrating the solution back.

TABLE I. Experimental Results

No. of runs	Temperature °C							Inflow rate of $N_2-H_2$ -mixture cc NTP/hr.	Outflow rate $N_A$ of $NH_3$ cc NTP/hr.
	$t_1$	$t_2$	$t_3$	$t_4$	$t_5$	$t_6$	$t_{average}$		
1	301	301	301	301	300	300	301	63600	5.16
2	301	301	301	300	300	300	301	79200	5.94
3*)	298	297	297	304	303	303	300	94200	6.18 ±0.22
4	302	302	302	300	300	300	301	106800	6.12 ±0.33
15	303	302	301	308	303	302	303	188400	5.22 ±0.21
5	353	353	353	354	354	354	354	51600	14.76 ±0.37
6	354	354	354	353	353	353	354	103200	20.46
16	353	353	353	357	357	357	355	178800	14.04 ±0.41
17*)	355	355	355	360	356	354	356	249000	18.78 ±0.47
7	406	406	403	403	403	403	404	79200	48.84
8	403	403	403	401	401	401	402	117600	62.22
9	404	404	404	405	405	405	405	55800	44.40
18	405	403	400	408	404	402	404	261600	58.68
22	403	403	403	407	406	405	405	61800	41.28
10	457	457	457	458	458	458	458	63600	102.90
11*)	459	458	458	454	454	454	456	120600	171.6
12)	456	457	457	458	458	458	458	82800	121.86
13	458	458	458	456	456	456	457	58200	99.36
14	463	460	453	460	458	452	458	273600	247.8
19	459	458	457	457	456	452	457	174000	164.28
20	458	458	458	458	458	458	458	79200	111.72
21	457	457	457	460	460	460	459	66000	99.36

\*) Temperature fluctuation in these runs is kept within  $\pm 4^\circ C$ , whereas that in other runs within  $\pm 2^\circ C$ .

\*\*\*) The probable relative errors of  $N_A$  are within 1.6% unless otherwise stated.

## § 5 Experimental results

The experimental results are shown in Table 1. *No.* of runs shows the order of runs, in which they have been conducted sporadically at different temperatures, in order to keep check with the activity of the catalyst. Temperatures  $t_1$ ,  $t_2$  and  $t_3$  are those read at the top, middle and bottom along the axis of  $R_s$  respectively and  $t_4$ ,  $t_5$  and  $t_6$  are those read respectively at the corresponding position on the wall. Ammonia outflow rate,  $N_A$ , given in Table 1 is the average value of the several measurements at the steady state for each run, its probable relative error being within 1.6% unless otherwise stated.

## § 6 Analysis for the rate of synthesis

The rate  $V$  of ammonia synthesis was determined in cc NTP of ammonia synthesized per hr per cc of the catalyst bed by analyzing the steady rate  $N_A$  of ammonia formation under the following premises :

- (I) The flow of gas components and the conversion among them are steady everywhere in  $R_s$ .
- (II) The temperature and the flow rate of every gas component are homogeneous over any cross section of  $R_s$ .
- (III) The mol fraction  $x^\delta$  of a gas component  $\delta$  equals its fraction of the flow rate.
- (IV) The temperature is homogeneous along the axis of  $R_s$ .

We have immediately from (1) and the premise (I)

$$n^A = 2(n_0^N - n^N) = (2/3)(n_0^H - n^H), \quad (6.1)$$

where  $n^\delta$  is the flow rate of gas component  $\delta$  across a horizontal section of  $R_s$ ,  $n_0^\delta$  that at the inlet and the superfix  $A$ ,  $N$  and  $H$  specify the gas components  $\delta$  for ammonia, nitrogen and hydrogen respectively. From the premise (III) the mol fraction  $x^A$  of ammonia at the horizontal section is given as

$$x^A = n^A / (n^A + n^N + n^H). \quad (6.2)$$

Eliminating  $n^N$  and  $n^H$  from (6.1) and (6.2), we have

$$x^A = n^A / (n_0 - n^A),$$

or

$$n^A = x^A n_0 / (1 + x^A), \quad (6.3. a)$$

where

$$n_0 = n_0^N + n_0^H. \quad (6.3. b)$$

The overall rate  $V$  is now homogeneous over any horizontal section of  $R_s$  as a function of temperature and concentrations  $x^A$  of components. The increment  $dn^A$  of the steady flow rate of ammonia through a horizontal section with the shift  $dh$  of the section along the direction of the flow is given as

$$dn^A = VSdh, \quad (6.4)$$

where  $S$  is the area of the section. We have, hence, by (6.3.a)

$$n_0 dx^A / (1 + x^A)^2 = VSdh \quad (6.5)$$

or by integration

$$\int_0^{x_t^A} dx^A / (1 + x^A)^2 V = v/n_0, \quad (6.6)$$

where  $v$  is the total volume of the catalyst bed and  $x_t^A$  is the mol fraction of ammonia in the outflow gas.

### § 7 Rate equation of ammonia synthesis

It was concluded by TOYOSHIMA and HORIUTI<sup>(1)(2)</sup> as mentioned in the introduction that the rate-determining step of decomposition of ammonia was (2.I) and that the unidirectional rate  $\bar{V}$  of decomposition was proportional to the ammonia partial pressure besides depending on the partial pressure of nitrogen. Under the present experimental condition, where the partial pressures of nitrogen and hydrogen are kept practically constant,  $\bar{V}$  must then be a sole function of the partial pressure of ammonia, the former being directly proportional to the latter.

The forward unidirectional rate  $\bar{V}$  is determined as follows. The right-hand side of (3) is developed as

$$(a^R/a^L K)^{1/\nu(r)} = \left\{ (a^A/a_e^A)^2 (a_e^H/a^H)^3 (a_e^N/a^N) \right\}^{1/\nu(r)}$$

noting that

$$a^R \equiv (a^A)^2, \quad a^L \equiv a^N (a^H)^3, \quad K = (a_e^A)^2 / a_e^N (a_e^H)^3, \quad (7.1)$$

where  $a^A$  etc. are activities of ammonia etc. and suffix  $e$  signifies the quantities at equilibrium as in what follows. We have, admitting the proportionality of the activities respectively to the relevant partial pressures  $P^A$  etc.,

$$(a^R/a^L K)^{1/\nu(r)} = \left\{ (P^A/P_e^A)^2 (P_e^H/P^H)^3 (P_e^N/P^N) \right\}^{1/\nu(r)}$$

or identifying  $P^H$  and  $P^N$  with  $P_e^H$  and  $P_e^N$  because of the practical constancy of  $P^H$  and  $P^N$

$$(a^R/a^L K)^{1/\nu(r)} = (P^A/P_e^A)^{2/\nu(r)}. \quad (7.2)$$

Since  $\nu(r)=2$ , we have  $(a^R/a^L K)^{1/\nu(r)}=P^A/P_e^A$ , or according to (3), that  $\bar{V}$  is independent of  $P^A$ , for  $\bar{V}$  is directly proportional to  $P^A$ , as mentioned above. The constant  $\bar{V}$  must of course equal  $\bar{V}_e$ .

Eq. (4) is given, on the other hand, by (7.2), as

$$V = \bar{V} (1 - P^A/P_e^A). \quad (7.3)$$

Substituting  $V$  from (7.3) into (6.6), we have on integration, identifying  $x^A$  with  $P^A$  by virtue of 1 atm. total pressure and ignoring  $x^A$  compared with unity,

$$-(S.V.) \ln(1 - E_f) = k, \quad (7.4)$$

where

$$(S.V.) = n_0/v, \quad E_f = P_i^A/P_e^A, \quad k = \bar{V}/P_e^A, \quad (7.5.S), (7.5.E), (7.5.k)$$

$P_i^A$  is  $P^A$  in the outflow gas,  $(S.V.)$  the space velocity and  $E_f$  the efficiency. Both the sides of (7.4) must be constant at constant temperature independent of  $(S.V.)$  according to (7.5.k), since  $\bar{V}$  is constant.

### § 8 The rate equations by other authors

TEMKIN and PYZHEV<sup>5)</sup> formulated the forward unidirectional rate of the catalyzed synthesis as

$$\bar{V} = k_a P^N \{ (P^H)^3 / (P^A)^2 \}^{g/f}, \quad (8.1. \bar{V})$$

assuming the rate-determining step to be the adsorption of nitrogen molecule, where  $g/f$  is a constant. They found 1/2 for the value of  $g/f$ , by fitting the above equation to the experimental results of themselves<sup>5)</sup>, WINTER<sup>12)</sup> and LARSON and TOUR<sup>13)</sup>. It follows from (8.1.  $\bar{V}$ ), (4) and (7.2), for  $\nu(r)=1$  of the assumed rate-determining step<sup>\*</sup>,

$$V = k_a \frac{P^N (P^H)^{3/2}}{P^A} \{ 1 - (P^A/P_e^A)^2 \}$$

or

$$V = k_T \{ 1 - (P^A/P_e^A)^2 \} (P_e^A)^2 / P^A, \quad (8.1. V)$$

where

$$k_T = k_a P^N (P^H)^{3/2} / (P_e^A)^2 \quad (8.1. k)$$

is a constant at the condition of the present experiment, where  $P^N$  and  $P^H$  are

\* ) The  $\bar{V}$  and  $\bar{V}$  advanced by TEMKIN and PYZHEV (Ref. 5) lead to an identical expression of  $V = \bar{V} - \bar{V}$ .

practically constant. Substituting  $V$  from (8.1.  $V$ ) into (6.6), we have by a similar integration to that in §7

$$-(S. V.) \ln(1 - E_f^2) = k_T. \quad (8. 2)$$

LOVE and EMMETT<sup>7)</sup>, on the other hand, concluded that

$$\bar{V} = k_2(P^A)^{0.60}/(P^H)^{0.85} \quad (8. 3)$$

from their experimental result on the decomposition of ammonia in the presence of doubly promoted iron catalyst (*No.* 931), hence that the rate-determining step was (2.I). It follows from (3), (7.2) and (8.3), putting  $\nu(r)=1$  for the concluded rate-determining step, that

$$\bar{V} = k_1(P^A)^{-1.40}, \quad (8. 4. V)$$

where

$$k_1 = k_2(P_e^A)^2(P^H)^{-0.85}. \quad (8. 4. k)$$

The  $V = \bar{V} - \bar{V}$  is expressed by (8.4) and (8.3) as

$$V = k_1(P^A)^{-1.40} \{1 - (P^A/P_e^A)^2\}.$$

Substituting  $V$  from the above equation into (6.6) and intergrating similarly as above, noting that  $k_1$  as given by (8.4.k) is practically constant at the present experimental condition, we have

$$(S. V.) \left\{ \sum_{l=0}^{\infty} E_f^{2.4+2l} / (2.4 + 2l) \right\} = k_E \quad (8. 5)$$

where

$$k_E = k_1/(P_e^A)^{2.4}.$$

### §9 Examination of the rate equation

The rate equation (7.4) is now examined for its validity with regard to the premises (I), (II), (III) and (IV) in §6, on which it is based.

We may take (I) for granted on the ground of sufficiently steady value of  $N_A$  as observed and (II) too, as supported by the practical coincidence of the observed temperatures at the every horizontal section through the catalyst bed as seen from Table 1. It is inferred in the previous analysis<sup>1)</sup> that (III) holds practically exactly at linear flow rate of gas above 0.06 cm/sec, which is amply satisfied at the present experimental series conducted at the linear flow rates above 3.5 cm/sec.

The premise (IV) is also practically satisfied within experimental errors of temperature determination except in a few runs as seen in Table 1. The value

$k_m$  of  $k$  at a specified temperature  $T_m$  supposed to be kept constant throughout the catalyst bed was evaluated as detailed in *Appendix* from the experimental result of run 14, admitting the premises (I), (II) and (III) but allowing for the temperature variation along the axis of the catalyst bed. The value of  $k_m$  thus obtained for  $T_m=731^\circ\text{K}$  from the experimental results of run 14 is shown in parentheses in Table 2. The  $k$ -value given right above for the same run is, similarly to other  $k$ -values given in the Table, that calculated by (7.4) assuming the validity of (IV) at the average temperature of  $t_1, \dots, t_6$ , which is identical with the above value of  $T_m$ . The approximate value of  $k$  thus obtained differs from  $k_m$  only by less than 1%. It may safely be taken that  $k$  in other cases calculated similarly by (7.4) is accurate enough in this regard, the variation of temperature along the axis being much smaller than in run 14 as seen from Table 1. No detailed examination of this sort has been tried for other constants  $k_T$  etc. expecting that the similar would be the case.

### § 10 Constancy of the rate constants

The values of  $k_T$  and  $k_E$  are calculated by (8.2) and (8.5) as shown in Table 2 side by side with  $k$ -values computed by (7.4). The values of  $P_e^A$  are calculated by the empirical equation of the equilibrium constant of the ammonia synthesis reaction given by GILLESPIE and BEATTIE<sup>10</sup>. The efficiency  $E_f$  is evaluated by (7.5.E), identifying  $P_t^A$  with the fraction  $N_A/n_0$  of the flow rate of ammonia on the ground of (III), §6 and of the one atm. total pressure at the present experiment. As shown in the columns 6, 7 and 8 of Table 2,  $k$  is appreciably constant at the respective constant temperatures with the average deviations of from 5.5 to 14.5%, whereas  $k_T$  and  $k_E$  varies by a factor of from 2 to 6. The  $k$ -value indicates, moreover, a considerable reproducibility of the activity of the one and the same catalyst sample used, with reference to the numbers of runs scattered sporadically over different temperatures.

### § 11 Discussion

ENOMOTO and HORIUTI<sup>9</sup> have previously shown that the rate  $V$  of the catalyzed synthesis of ammonia near equilibrium is proportional to  $P_e^A - P^A$  at the experimental condition, where the partial pressures of nitrogen and hydrogen are kept practically constant as in the present case and that the appropriate proportionality constant,  $r_1 := V/(P_e^A - P^A)$  is given as  $r_1 = 2\bar{V}_e/\nu(r)P_e^A$ . They have determined  $r_1$  at different temperatures from  $400^\circ\text{C}$  to  $445^\circ\text{C}$  from the observed increase or decrease of ammonia partial pressure with time in the presence of the catalyst of the same preparations as used in the present experiment, hence

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TABLE 2. The rate constants of ammonia synthesis from the present experimental results.

Temperature °C	$P_e^4$ atm. $\times 10^2$	No. of runs	(S.V.) $\frac{\text{cc NTP}}{\text{cc cat. hr.}}$	$E_f$	$k$ $\frac{\text{cc NTP}}{\text{cc cat. hr.}}$	$k_T$ $\frac{\text{cc NTP}}{\text{cc cat. hr.}}$	$k_E$ $\frac{\text{cc NTP}}{\text{cc cat. hr.}}$
301	1.89	1	1320	$4.2 \times 10^{-3}$	5.56	$2.33 \times 10^{-2}$	$1.10 \times 10^{-3}$
		2	1644	$4.0 \times 10^{-3}$	6.60	$2.63 \times 10^{-2}$	$1.19 \times 10^{-3}$
		3	1955	$3.47 \times 10^{-3}$	6.78	$2.35 \times 10^{-2}$	$1.00 \times 10^{-3}$
		4	2218	$3.08 \times 10^{-3}$	6.72	$2.03 \times 10^{-2}$	$0.862 \times 10^{-3}$
		15	3910	$1.5 \times 10^{-3}$	5.87	$0.90 \times 10^{-2}$	$0.270 \times 10^{-3}$
355	0.777	5	1070	$3.68 \times 10^{-2}$	40.1	1.45	0.162
		6	2140	$2.55 \times 10^{-2}$	55.2	1.39	0.135
		16	3710	$1.01 \times 10^{-2}$	37.6	0.378	0.225
		17	5170	$0.971 \times 10^{-2}$	50.2	0.487	0.0304
404	0.384	7	1644	0.161	288	43.2	8.60
		8	2440	0.138	353	46.9	8.96
		9	1158	0.207	269	50.6	11.0
		18	5430	0.0584	326	18.6	2.48
		22	1282	0.174	245	49.3	8.20
458	0.195	10	1320	0.830	2340	1530	623
		11	2500	0.729	3270	1900	715
		12	1717	0.756	2420	1450	560
		13	1208	0.875	2520	1760	898
		14	5680	0.464	3550 (3530)	1370	427
		19	3610	0.484	2390	960	304
		20	1644	0.723	2110	1210	459
		21	1370	0.773	2030	1250	486

found that  $RT^2 d \ln r_1 / dT = 33$  Kcal. It follows from the preceding expression of  $r_1$  and (7.5.k) that  $r_1$  varies with temperature proportional to  $k$ , inasmuch as  $\bar{V}$  in (7.5.k) equals  $\bar{V}_e$  as mentioned in §7. Therefore,  $RT^2 d \ln k / dT$  is required to be identical with  $RT^2 d \ln r_1 / dT$ , provided that the reaction (1) were followed consistently both in the cases.  $RT^2 d \ln k / dT$  is now  $31.9 \pm 1.1$  Kcal as determined from the values of  $k$  at different temperatures in Table 2, which agrees satisfactorily with the above value of  $RT^2 d \ln r_1 / dT$ , fulfilling the requirement.

Table 3 shows the  $k$ -value calculated from the recent data of OZAKI, TAYLOR and BOUDART<sup>15)</sup> by (7.4), which is not as constant as that from the present experiment. Both the series of experiments have been carried out under almost the same experimental condition in the presence of the same sort

TABLE 3. The  $k$ -values calculated from the data by OZAKI TAYLOR, and BOUDART<sup>15)</sup>.

Temperature °C	$P_e^A$ atm. $\times 10^2$	(S. V.) cc NTP cc cat. hr.	$P_f^A$	$E_f$	$k$ cc NTP cc cat. ha.
302*)	1.86**)	3880	$4.5 \times 10^{-3}$	0.242	1075
		4000	$4.5 \times 10^{-3}$	0.242	1107
		6417	$3.78 \times 10^{-3}$	0.203	1453
		6533	$3.65 \times 10^{-3}$	0.196	1424
		8533	$3.25 \times 10^{-3}$	0.175	1637
		8767	$3.3 \times 10^{-3}$	0.177	1705
		10100	$3.05 \times 10^{-3}$	0.164	1806
		11900	$2.85 \times 10^{-3}$	0.153	1975
		12833	$2.75 \times 10^{-3}$	0.148	2066
		13333	$2.8 \times 10^{-3}$	0.151	2180
278*)	2.88**)	3967	$3.05 \times 10^{-3}$	0.106	444
		6667	$2.5 \times 10^{-3}$	0.0869	606
		8767	$2.25 \times 10^{-3}$	0.0782	714
		8767	$2.15 \times 10^{-3}$	0.0747	682
		10433	$2.1 \times 10^{-3}$	0.0730	791
		11933	$1.9 \times 10^{-3}$	0.0660	815
		13333	$1.88 \times 10^{-3}$	0.0653	900
		302	1.86	4333	$2.38 \times 10^{-3}$
		7033	$1.95 \times 10^{-3}$	0.105	780
		7033	$1.9 \times 10^{-3}$	0.102	756
		9266	$1.75 \times 10^{-3}$	0.0942	917
		11100	$1.65 \times 10^{-3}$	0.0887	1025
		12833	$1.55 \times 10^{-3}$	0.0834	1115
		14500	$1.45 \times 10^{-3}$	0.0779	1176
251*)	4.83**)	3966	$1.9 \times 10^{-3}$	0.0394	159
		6533	$1.5 \times 10^{-3}$	0.0311	206
		8533	$1.35 \times 10^{-3}$	0.0279	241
		10433	$1.2 \times 10^{-3}$	0.0249	263
		12833	$1.1 \times 10^{-3}$	0.0228	302
278	2.88	4283	$1.65 \times 10^{-3}$	0.0574	253
		4450	$1.6 \times 10^{-3}$	0.0555	254
		7100	$1.35 \times 10^{-3}$	0.0469	310
		9267	$1.15 \times 10^{-3}$	0.0399	377
		11100	$1.13 \times 10^{-3}$	0.0342	444
		14533	$1.00 \times 10^{-3}$	0.0349	517

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Temperature °C	$P_2^A$ atm. $\times 10^2$	(S. V.) * cc NTP cc cat. hr.	$P_2^A$	$E_f$	$k$ cc NTP cc cat. hr.
251	4.83	4283	$1.0 \times 10^{-3}$	0.0207	89.6
		4450	$0.95 \times 10^{-3}$	0.0197	88.2
		7233	$0.8 \times 10^{-3}$	0.0166	121
		9267	$0.7 \times 10^{-3}$	0.0145	135
		9533	$0.7 \times 10^{-3}$	0.0145	139
		11500	$0.65 \times 10^{-3}$	0.0135	156
		12833	$0.62 \times 10^{-3}$	0.0128	165
		14833	$0.59 \times 10^{-3}$	0.0122	182
218*)	9.33**)	6666	$0.61 \times 10^{-3}$	$6.54 \times 10^{-3}$	49.0
		10400	$0.49 \times 10^{-3}$	$5.25 \times 10^{-3}$	55.0
		13333	$0.43 \times 10^{-3}$	$4.61 \times 10^{-3}$	62.3
302*)	1.86**)	1757	$5.5 \times 10^{-3}$	0.296	617
		2383	$4.8 \times 10^{-3}$	0.258	712
		3750	$3.95 \times 10^{-3}$	0.212	893
		4900	$3.55 \times 10^{-3}$	0.191	936
		6960	$3.05 \times 10^{-3}$	0.164	1245
302	1.86	1907	$2.80 \times 10^{-3}$	0.151	312
		2467	$2.55 \times 10^{-3}$	0.137	363
		2467	$2.5 \times 10^{-3}$	0.135	357
		4067	$2.15 \times 10^{-3}$	0.116	502
		5367	$1.85 \times 10^{-3}$	0.0995	563
		7767	$1.63 \times 10^{-3}$	0.0874	710

\*) Data of reaction  $N_2 + 3D_2 = 2ND_3$ .

\*\*) These values were calculated as  $\sqrt{K P^N (P^D)}$  from  $P^N$ , the partial pressure  $P^D$  of deuterium gas and the equilibrium constant  $K$  of the reaction (1) for protium gas, the corresponding equilibrium constant for deuterium not being found in literature. The relative variation of the calculated value of  $k$  could hardly be affected by this approximation as seen from (7.4) in case where  $E_f$  was small as compared with unity.

of catalyst, *i.e.* doubly promoted catalyst, except that the catalyst was reduced at 550°C in the present experiment, whereas at 400°C in that of TAYLOR *et al.*<sup>15)</sup> This situation might be responsible for the above difference.

The constancy of  $k$  supported by the reproducibility in the present experiment confirms the underlying propositions that  $\nu(r)=2$  and that  $\bar{V}$  is independent of ammonia partial pressure at the present experimental condition. These propositions are deduced from the previous conclusion of TOYOSHIMA and HORIUTI<sup>2)</sup>, that  $\bar{V}$  was governed by (2.I) and proportional to the ammonia

partial pressure, which was arrived at from the experimental result with the catalyst of the same preparation as that of the present experiment.

The latter group of authors concluded besides that  $\bar{V}$  depends on the partial pressure of nitrogen as mentioned in the introduction. This conclusion is beyond the scope of present investigation, where the partial pressure of nitrogen is practically fixed. However, LOVE and EMMETT<sup>7)</sup> have concluded from the observed indifference of catalyzed decomposition rate of ammonia to the diluent either of nitrogen or of helium, that the rate of controlling step of the decomposition is unaffected by the nitrogen partial pressure. These conflicting conclusions will be the subject of our further investigations.

### Summary

(1) The 1:3 nitrogen-hydrogen mixture was allowed to flow through the bed of doubly promoted iron catalyst at 1 atm. total pressure and at different temperatures from 301 to 458°C. The catalyst was reduced at temperature raised stepwise up to 550°C. The ammonia outflow rate, hence the efficiency  $E_f$  of ammonia formation was determined at each constant temperature for different space velocity ( $S. V.$ ) ranging from 1000 to 5700 cc NTP/cc catalyst hr.

(2) The rate equation  $-(S. V.) \ln(1 - E_f) = k$  of ammonia synthesis, where  $k$  is constant independent of ( $S. V.$ ) at constant temperature, was deduced from the premises *A*) that partial pressures of nitrogen and hydrogen are respectively constant and *B*) that the stoichiometric number of the rate-determining step is 2 and the unidirectional decomposition rate of ammonia is proportional to its partial pressure. The premise *A*) was practically realized experimentally, whereas *B*) was derived from the previous conclusion of ENOMOTO, HORIUTI and KOBAYASHI<sup>3)4)</sup> and HORIUTI and TOYOSHIMA<sup>2)</sup>.

(3) The rate constant  $k$  was found to be remarkably reproducible and constant over the range of space velocity mentioned at the respective constant temperatures, whereas the similar constants as required by other rate laws varied considerably.

(4) The activation energy  $RT^2 d \ln k/dT$  was found to be  $31.9 \pm 1.1$  Kcal, which was in excellent agreement with that 33 Kcal derived from independent measurements by ENOMOTO and HORIUTI<sup>3)</sup> with the catalyst of the same preparation.

(5) These results verify the previous conclusions of HORIUTI and TOYOSHIMA<sup>2)</sup> underlying the rate equation mentioned in (2), that the rate-determining step of the catalyzed decomposition of ammonia was the step of the decomposition of adsorbed imino group and that the unidirectional rate of decomposition

was proportional to the partial pressure of ammonia.

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APPENDIX

The value  $k_m$  of  $k$ , which would be obtained at  $T_m = 731^\circ K$  supposed to be kept constant over the catalyst bed, was worked out as follows, allowing for the variation of temperature along the axis of the catalyst bed, on the basis of the premises (I), (II) and (III) particularly for run 14 shown in Table 2.

Identifying  $x^A$  with  $P^A$  but ignoring it as compared with unity as in the text, we have from (6.5)

$$n_0 dP^A = VS dh,$$

or substituting  $V$  from (7.3)

$$n_0 dP^A = \bar{V} (1 - P^A/P_e^A) S dh. \quad (\text{i})$$

The  $\bar{V}$  in (i) is given as a function of temperature as

$$\bar{V} = \bar{V}_m \exp \left\{ (E/R)(1/T_m - 1/T) \right\}, \quad (\text{ii. a})$$

where

$$E = 19.3 \pm 1.1 \text{ Kcal.} \quad (\text{ii. b})$$

Eq. (ii) was deduced, according to (7.5.k), from  $k$ -values at different temperatures as determined by (7.4) without allowing for the temperatures variation along the axis and from the known function  $P_e^A$  of temperature, *i. e.*

$$P_e^A = P_{e,m}^A \exp \left\{ (\Delta H/R)(1/T_m - 1/T) \right\}, \quad (\text{iii. a})$$

where

$$\Delta H = -12.6 \text{ Kcal, } P_{e,m} = 0.195 \times 10^{-2} \text{ atm} \quad \text{for } T_m = 731^\circ K; \quad (\text{iii. b}), (\text{iii. c})$$

(iii) was derived for 1 atm. total pressure from the equilibrium constant given by GILLESPIE and BEATTIE<sup>14)</sup>.

The temperature along the axis of the catalyst bed is given by experiment as a function of  $h$ , hence  $\bar{V}$  and  $P_e^A$  are given as functions of  $h$  according to (ii) and (iii); the differential equation (i) is in consequence integrated to give  $\bar{V}_m$  as a function of the value  $P_i^A$  of  $P^A$  at the outlet. The value of  $\bar{V}_m$  is thus determined by the directly observed value of  $P_i^A$ . The value of  $k_m$  in question is now given by (7.5.k) as

$$k_m = \bar{V}_m / P_{e,m}^A. \quad (\text{iv})$$

Practically the above calculation has been carried out as follows by introducing the independent variable  $l$ , *i. e.*

$$l = h/H, \quad (\text{v})$$

where  $H$  is the height of the catalyst bed.  $\bar{V}$  and  $P_e^A$  are now known functions of  $l$ , since they are given as known functions of  $h$  as mentioned above; the differential equation (i) is hence written in the form

$$\frac{n_0}{SH} \frac{dP^A(l)}{dl} + \frac{\bar{V}(l)}{P_e^A(l)} P^A(l) - \bar{V}(l) = 0,$$

which is integrated as

$$P_t^A = \int_0^1 \exp\left(\int_1^l \frac{SH}{n_0} \frac{\bar{V}(l)}{P_e^A(l)} dl\right) \frac{SH}{n_0} \bar{V}(l) dl, \quad (\text{vi})$$

referring to the boundary condition that  $P^A=0$  at  $l=0$ . The integral is evaluated by developing  $l$  as

$$l = a + b/T + c/T^2, \quad (\text{vii. a})$$

where the constants  $a$ ,  $b$  and  $c$  are fitted to the experimental data of run 14 in question, *i. e.*  $(t_3 + t_0)/2 = 452.5^\circ\text{C}$  at  $l=0$ ,  $(t_2 + t_5)/2 = 459^\circ\text{C}$  at  $l=1/2$  and  $(t_1 + t_4)/2 = 461.5^\circ\text{C}$  at  $l=1$ , as

$$a = 7.490437 \times 10^3, \quad b = -1.087609 \times 10^7, \quad c = 3.948013 \times 10^9 \quad (\text{vii. b})$$

The integral  $\int_1^l \frac{\bar{V}(l)}{P_e^A(l)} dl$  in (vi) is carried out by (vii. a), (ii. a) and (iii. a)

as

$$\int_1^l \frac{\bar{V}(l)}{P_e^A(l)} dl = \frac{\bar{V}_m}{P_{e,m}^A} \exp\left(\frac{E - \Delta H}{RT_m}\right) \left[ \frac{R}{\Delta H - E} \left\{ e^{\frac{\Delta H - E}{RT_i}} \left(b + \frac{2c}{T}\right) - e^{\frac{\Delta H - E}{RT_i}} \left(b + \frac{2c}{T_i}\right) \right\} + 2 \left(\frac{R}{\Delta H - E}\right)^2 c \left(e^{\frac{\Delta H - E}{RT_i}} - e^{\frac{\Delta H - E}{RT}}\right) \right], \quad (\text{viii})$$

where  $T_i$  is the particular value of  $T$  at  $l=1$ . The integrand of (vi) is now plotted against  $l$  with  $T$  as a parameter with reference to (ii. b), (iii. b), (iii. c), (vii. b) and (viii) for a trial value of  $\bar{V}_m$  at  $T_m = 731^\circ\text{K}$ . The graphical integration of (vi) yields a trial value of  $P_t^A$  relevant to that of  $\bar{V}_m$ . It is thus found that the value 6.87 cc NTP/cc cat. hr of  $\bar{V}_m$  fits in with the observed value of  $P_t^A$  given in Table 2, *i. e.*

$$P_t^A = 9.06 \times 10^{-4} \text{ atm.}$$

The  $k_m$ -value of run 14 given in the parentheses of Table 2 is obtained from the above value of  $\bar{V}_m$  by (iv) and (iii. c).