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DETERMINATION OF STOICHIOMETRIC NUMBER OF AMMONIA SYNTHESIS REACTION AT 29.5 ATM.

By

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Introduction

ENOMOTO and HORIUTI[1] have previously found experimentally that the stoichiometric number of the rate-determining step of the catalysed ammonia synthesis reaction,

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

in the presence of commercial synthesis catalyst at ordinary pressure is 2 and, assuming that reaction (1) proceeded through the sequence of steps,

$$\left.\begin{array}{l} N_2 \longrightarrow 2N(a) \\ H_2 \longrightarrow 2H(a) \\ N(a) + H(a) \longrightarrow NH(a) \\ NH(a) + H(a) \longrightarrow NH_2(a) \\ NH_2(a) + H(a) \longrightarrow NH_3 \end{array}\right\} \qquad (2)$$

where (a) denoted adsorbed atom or group on the catalyst, concluded that the rate-determining step was one of last three steps of stoichiometric number 2 or occurring twice every overall reaction (1).

This conclusion was found in accordance with the result of kinetic analysis arrived at by HORIUTI and TOYOSHIMA[2] later to be published.

The similar determination was now conducted at higher pressure 29～30 atm., which was practicable in our laboratory, it being desirable for discussing the mechanism of synthesis in commercial plant at several hundred atmospheric pressures.

The principle of the determination, the experiments conducted and the results obtained are detailed in the following sections.

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1) ENOMOTO and HORIUTI, J. Res. Inst. Catalysis, Hokkaido University, 2, 87 (1953).

2) HORIUTI and TOYOSHIMA, published later.

§ 1. Principle of The Stoichiometric Number Determination

The experimental determination of the stoichiometric number n of the rate-determining step is based as in the previous paper[1] on the general kinetic equation,

$$V_S = \overrightarrow{\mathfrak{V}} \left\{1 - \exp\left(\frac{\Delta\mu}{nRT}\right)\right\} \tag{2}$$

derived by one of present authors,[3] where V_S is the steady rate of the overall reaction, $\overrightarrow{\mathfrak{V}}$ the forward rate of the rate-determining step multiplied by its stoichiometric number n, i. e., the forward rate of the overall reaction, $\Delta\mu$ the excess of the sum of chemical potentials of the resultants over that of the reactants of the overall reaction and RT of usual meaning.

Expressing $\Delta\mu$, as,

$$\Delta\mu = RT \log \frac{(P^{\mathrm{NH_3}})^2}{K P^{\mathrm{N_2}} (P^{\mathrm{H_2}})^3} \tag{3}$$

where K is the equilibrium costant, i. e,

$$K = \frac{(P_e^{\mathrm{NH_3}})^2}{P_e^{\mathrm{N_2}} (P_e^{\mathrm{H_2}})^3} \tag{4}$$

suffix e denoting the quantities at equilibrium, and writing partial pressures $P^{\mathrm{NH_3}}$ etc. in terms of total pressure P and mol fraction x of ammonia, assuming 1 : 3 ratio of $P^{\mathrm{N_2}}$ and $P^{\mathrm{H_2}}$, as,

$$P^{\mathrm{NH_3}} = Px \tag{5. $\mathrm{NH_3}$}$$

$$P^{\mathrm{H_2}} = \frac{3}{4} P(1-x) \tag{5. $\mathrm{H_2}$}$$

$$P^{\mathrm{N_2}} = \frac{1}{4} P(1-x) \tag{5. $\mathrm{N_2}$}$$

we have from (2), (3), (4) and (5),

$$V_S = \overrightarrow{\mathfrak{V}} \left[1 - \left\{\frac{x^2}{K' P^2 (1-x)^4}\right\}^{1/n}\right] \tag{6. V}$$

where,

$$K' = 3^3 4^{-4} K \tag{6. K}$$

and,

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3) HORIUTI, J. Res. Inst. Catalysis, Hokkaido University, 1, 8 (1948).

$$\frac{x_e^2}{K' P_e^2 (1-x_e)^4} = 1 \tag{6. e}$$

V_S is, on the other hand, equated to the increasing rate of ammonia partial pressure Px or to the decreasing rate of P, according to the stoichiometric relation (1) as,

$$V_S = \frac{d}{dt}(Px) = -\dot{P} \tag{7. V}$$

so that,

$$\dot{x} = \frac{1+x}{P} V_S \tag{7. x}$$

or

$$\frac{dP}{dx} = -\frac{P}{1+x} \tag{7. P}$$

Eq. (6. V) is now expressed according to (7. x) as,

$$\dot{x} = \frac{1+x}{P} \vec{\mathfrak{R}} \left\{1 - \frac{x^{2/n}}{K'^{1/n} P^{2/n} (1-x)^{4/n}}\right\} \tag{8}$$

Expanding the right of the above equation in the neighbourhood of x_e, where it vanishes according to (6. e) and neglecting terms higher than the second order, we have, referring to (7. P) and (5. NH_3),

$$-\dot{x} = r_1 (x - x_e) \tag{9. x}$$

where

$$r_1 = \frac{2}{n} \frac{\vec{\mathfrak{R}}_e}{P_e^{NH_3}} \frac{1+3x_e}{1-x_e} \tag{9. r_1}$$

The r_1 and x_e may be determined by adapting (9. x) or its integrated form,

$$\log |x - x_e| = -r_1 t + \text{const} \tag{10}$$

to observed x varying with t in the neighbourhood of equilibrium just as in the previous paper.[1] The stoichiometric number n of the rate-determining step is now determined according to (9. r_1) by observing further $\vec{\mathfrak{R}}_e$ by means of nitrogen isotope.

In the following sections will be described materials, apparatus, procedure and results of experiment for determining r_1 and $\vec{\mathfrak{R}}_e$ according to the above.

§ 2. Materials

The 1 : 3 nitrogen-hydrogen mixture termed 1 : 3 gas in what follows was prepared by passing ammonia from cylinder at 1 atm. in succession through ammonia synthesis catalyst kept at 550~600°C, a pack of lassig rings counter to a shower of cold water for removing undecomposed ammonia and then copper foil heated at 300°C for reducing contaminating oxygen to water. The gas mixture thus prepared was now compressed to 150 atm. and stored in cylinders. Before use the mixture was further passed through two layers of felt and a layer of alumina in-between for removing oil mist and moisture, a column of reduced copper powder kept at 300°C and that of reduced nickel supported on pumice kept at 300°C for reducing last trace of oxygen, a spiral pipe cooled by water for condensing water vapour, two columns of active alumina for drying and finally two columns of fused potassium hydroxide for removing carbon dioxide. The final gas was confirmed of 1 : 3 composition by analysis.

The catalyst used was, throughout the present experiments, one and the same sample of "Catalyst II" of the previous work[1], i. e., commercial doubly promoted one.

Normal and N^{15}-shifted ammonia were prepared and purified similarly as in the previous work.[1]

§ 3. Apparatus

Fig. 1 shows the apparatus used both for r_1- and $\mathfrak{R}_e$-determinations. R_1 is the reaction chamber of 280 cc capacity heated from outside by electric furnace F, in which 15 gm catalyst is supported as illustrated, on a parforated chrome-molybdenum steel plate. D is a blind tube of the same material of 3 mm inner diameter with a cap with a hole of 2 mm diameter, screwed at its top, through which an alumel-chromel thermo-junction was inserted at the catalyst by leads l_1 and l_2. P_1 and P_2 are pressure gauges respectively of 0.5 and 1.0 atm. division, V_1, V_2, V_3 valves capable of holding vacuum from several ten atm. and R_2 a gas reservoir of the same capacity as that of R_1, where gas mixture of known composition is prepared as seen later.

B is a glass flask of ca. 3 litres capacity for reserving ammonia communicated with glass manometer M through a glass cock C_2 and with vacuum line through cock C_7 and T_1 a trap used for introducing

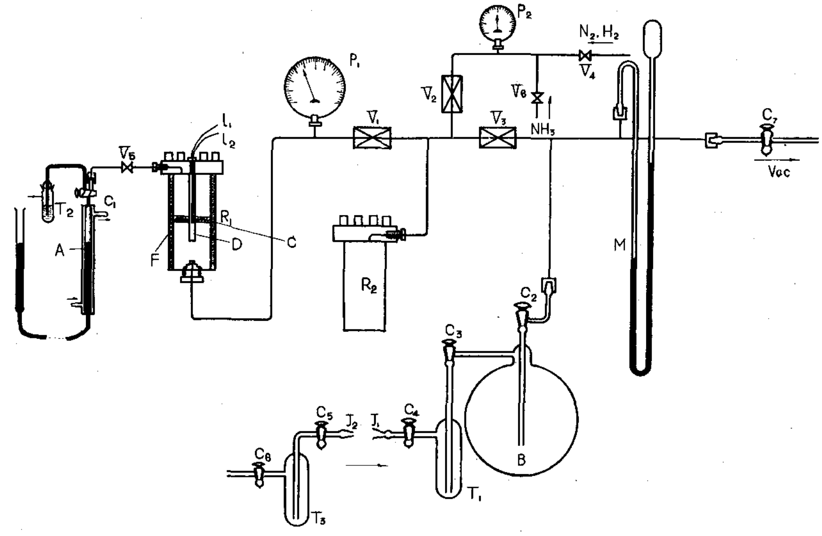

Fig. 1 Apparatus .

R_1 :—Reaction Chamber. F:—Electric Heater. C:—Catalyst.
A :—Gas Analyser. B :—Glass Flask. R_2 :—Gas Reservoir.
P_1, P_2:—Pressure Gauge. M :—Manometer. l_1, l_2: —Leads of Thermo-Junction.
V_1, V_2, V_3 :—Vacuum High Pressure Valves. V_5 :—Needle-Valve.
C_1, C_2, C_3, C_4, C_4, C_6, C_7 :—Glass Stopcocks.

into B a required amount of ammonia brought up from a separate vacuum system in trap T_3 attached to T_1 by joints J_1 and J_2.

These equipments are combined by iron pipe of 6 mm outer and 4 mm inner diameters and glass tubings illustrated respectively by single and double lines.

A is a gas burette surrounded by a water jacket and fitted with a double cock C_1, one of its branch being connected to the iron pipe from needle-valve V_5 with rubber tubing. T_2 is a trap containing dilute hydrochloric acid for fixing ammonia in the sampled gas in A for analysis.

§ 4. Reduction of Catalyst

The catalyst used for r_1- and $\mathfrak{R}_e$-determination was reduced *in situ* in R_1 as follows; 8 to 10 mesh even-grained catalyst in R_1 was kept at 450°C in a flow of 1 : 3 gas of 20 atm.～22 atm. pressure for 83 hrs, then at 500°C for 150 hrs. in the same flow and finally at the same temperature for 53 hrs. in a flow of cylinder hydrogen of the same pressure, purified through a train similar to that for 1 : 3 gas, until only a faint fringe of condensed water was perceptible on the wall of a liquid air trap one hour after the gas from the catalyst had been passed through it.

§ 5. Procedure of r_1-Determination

For determining r_1 in accordance with §1, x was followed with time t as below at pressures around 29.5 atm. at 450°, 475°, and 492°C respectively with one and the same catalyst throughout by means of the apparatus outlined in § 3.

After the catalyst was reduced as stated in the foregoing section, 1 : 3 gas was passed again at 20～22 atm. pressure for 1 hr. and the gas passed was confirmed of 1 : 3 composition by analysis. The gas was now purged down to atmospheric pressure, a new portion of 1 : 3 gas admitted to make up 31.5 atm. pressure at 450°C in R_1, the synthesis of the first series I thus started being followed by sampling occasionally 5 cc gas mixture into A at atmospheric pressure through V_5 and C_1 at recorded time after the start. The sampled gas was allowed to flow out through T_2, which contained 1 cc dilute hydrochloric acid for absorbing ammonia in the sample. The ammonia content of the sample was determined colorimetrically by means of Nessler reagent to work out mol fraction x of ammonia in the gas.

Synthesis thus being followed close up to equilibrium, the catalyst was subjected as follows to the preliminary treatment for the subsequent series II of decomposition for alternatively determining r_1 at the same temperature; the residual gas of Series I was purged down to the atmospheric pressure, the catalyst kept in a flow of ca. 100 cc NTP/min. rate of pure hydrogen and then of 1 : 3 gas each for one hr. at 20～22 atm. and at the temperature of the relevant series, i. e., 450°C in this case; this preliminary treatmant of the catalyst was followed before every admission of a fresh portion of gas over the catalyst for r_1- or $\mathfrak{R}_e$-determination.

The gas of the preliminary treatment was now purged again, the mixture of excess ammonia content then admitted from R_2 into R_1 at 29.5 atm. pressure and the decomposition thus started followed toward equilibrium quite similarly as in the synthesis. The mixture of excess ammonia content was prepared in R_2 as follows; T_3 filled with 0.07 mol ammonia was joined to the apparatus, T_1, B and the space inside C_5 evacuated through C_7, the content of T_3 distilled into T_1 with C_3 closed, allowed to evaporate into B and T_1 with C_2 and C_4 closed, collected instantly by condensation into preliminarily evacuated R_2 through C_2 and V_3 by cooling R_2 with liquid air,*) the condensate quickly evaporated in R_2 with V_1, V_2 and V_3 colsed and then 1 : 3 gas admitted through V_2 to make up 44.5 atm. pressure there as measured by P_2.

It was shown by a control experiment that a homogeneous mixture was obtained by the present procedure of mixing ammonia with 1 : 3 gas**) but not alternatively by that of admitting 1 : 3 gas into R_2 over condensed ammonia and subsequently evaporating the latter.

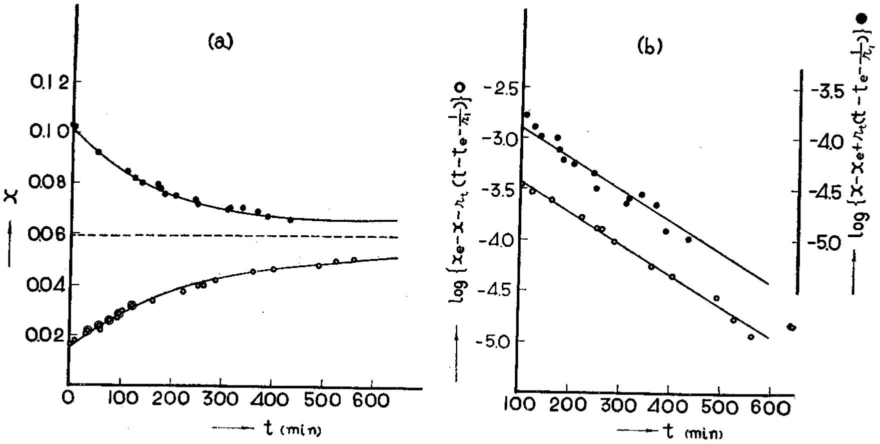

Fig. 2 r_1- and x_e-Observation .

Temperature :— 450 °C

○ :—Series I (sythesis). ● :—Series II (decomposition).

◎ :—Series III (synthesis).

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*) This procedure of instant condensation of vapour was preferred to the direct distillation from T_3 into R_2 for minimizing leakage referred to later.

**) Known amount of normal ammonia was mixed in R_2 with 1 : 3 gas according to the procedure in the text to make up 44.5 atm. there, its ammonia mol fraction being 4.3% by calculation. The gas was now expanded into R_1 kept at room temperature containing 1 : 3 gas at 1 atm. free from ammonia, to fill up the combined space of R_1 and R_2 at 30 atm. pressure.

If ammonia was homogeneously mixed in R_2 before communication, its mol fraction in R_1 must be either 0.042 or 0.043 according as the preoccupant in R_1 is mixed homogeneously with gas from R_2 only inside R_1 or whole throughout R_1 and R_2, the mol fraction lying in-between in the intermediate case.

The gas was now sampled three times in succession from R_1 into A and the ammonia mol fraction of samples determined at 0.043, 0.042 and 0.042 respectively in confirmation of the homogeneous mixing in R_2.

TABLE 1. Variation of Ammonia Mol Fraction with Time at 450°C

Series	Reaction Time t min.	Ammonia Mol Fraction x	Total Pressure atm.
I Synthesis	0	0.0162	31.5
	10	0.0180	
	31	0.0203	
	61	0.0219	
	92	0.0269	
	102	0.0296	29.9
	162	0.0338	
	222	0.0376	
	252	0.0398	
	262	0.0398	28.8
	287	0.0420	
	362	0.0452	
	402	0.0462	
	492	0.0478	
	526	0.0496	
	562	0.0505	27.0
II Decomposition	0	0.1028	29.5
	3	0.1022	
	50	0.0920	
	108	0.0845	
	125	0.0819	
	138	0.0800	
	170	0.0795	
	175	0.0774	
	184	0.0757	
	205	0.0750	
	245	0.0736	
	250	0.0717	
	310	0.0698	
	315	0.0702	
	340	0.0704	
	370	0.0690	
	390	0.0670	
	435	0.0660	27.2
III Synthesis (After $\vec{\mathfrak{K}}$-Determin. Table 6)	36	0.0214	31.5
	56	0.0237	
	76	0.0259	
	96	0.0283	
	122	0.0319	29.8

TABLE 2. Variation of Ammonia Mol Fraction with Time at 475°C

Series	Reaction Time t min.	Ammonia Mol Fraction x	Total Pressure atm.
IV Synthesis	0	0.0151	31
	20	0.0207	
	40	0.0271	
	60	0.0314	
	80	0.0344	
	120	0.0378	
	140	0.0404	
	165	0.0402	29.5
V Decomposition	0	0.0872	29.7
	7	0.0829	
	30	0.0767	
	40	0.0730	
	70	0.0663	
	100	0.0615	
	130	0.0583	29.4
VIII Synthesis	23	0.0202	31
	43	0.0266	
	63	0.0317	

TABLE 3 Variation of Ammonia Mol Fraction with Time at 492°C

Series	Reaction Time t min.	Ammonia Mol Fraction x	Total Pressure atm.
VI Synthesis	0	0.0177	31
	2	0.0195	
	22	0.0286	
	42	0.0324	
	62	0.0345	
	82	0.0343	30.2
VII Decomposition	0	0.0533	29.5
	12	0.0499	
	32	0.0450	
	52	0.0417	
	72	0.0432	
	112	0.0396	
	152	0.0390	29.0

After the completion of Series II of decomposition at 450°C described above, $\vec{\mathfrak{R}}_e$-determination at the same temperature was conducted as detailed later and then Series III of synthesis resumed at the same temperature for keeping check with the activity of the catalyst.

The synthesis and decomposition were similarly followed in Series IV (synthesis) and V (decomposition) at 475°C, then in VI (synthesis) and VII (decomposition) at 492°C in succession and finally the synthesis of Series VIII was at 475°C for further check of the catalyst's activity.

Table 1 to 3 show x as well as total pressure P observed against time t of each Series from I to VIII. The x, t relation of Table 1 is illustrated in Fig. 2, (a), which shows that results of Series I and III of synthesis practically fall in with each other; those of Series IV and VIII at 475°C doing the same, a satisfactory check was thus provided with the reproducibility of the catalyst's activity.

§ 7. Correction for Leakage

It has been observed in experiments of foregoing section as shown in Table 1 to 3 that the total pressure decreased not only in synthesis but in decomposition, when the total mol number should increase along with time, definitely indicating the leakage of gas.

Separate experiment has now been carried out, after the conclusion of measurements for r_1 and $\vec{\mathfrak{R}}_e$, for examining the effect of leakage on the evaluation of these quantities in the presence of the same catalyst and at the same temperatures as those in the above measuremcents by admitting the equilibrium mixture of ammonia and 1:3 gas into R_1 and by following with time the total pressure by means of P_1 as well as the ammonia mol fraction by analysis. Table 4 shows the result of the experiment at 450°C with the initial mol fraction $x_0=0.060$ of ammonia adjusted at equilibrium. We see from Table 4, that x remains constant within experimental errors, while the total pressure steadily decreases. It hence follows from the result in accordance with the relation,

$$-\left(\frac{\partial P}{\partial t}\right)_x = kP \qquad (11.P)$$

that,

$$k = (1.54 \pm 0.05) \times 10^{-4}\ \text{min.}^{-1}\ \text{at}\ 450^\circ\text{C} \qquad (11.k.\text{a})$$

Similar observations at 475°C and 492°C give,

$$k = (1.64 \pm 0.09) \times 10^{-4} \text{ min.}^{-1} \text{ at } 475^\circ\text{C} \qquad (11.k.\text{b})$$

$$k = (1.71 \pm 0.11) \times 10^{-4} \text{ min.}^{-1} \text{ at } 492^\circ\text{C} \qquad (11.k.\text{c})$$

The x, found incidentally constant in the above experiment, varies in general by the different rate of leakage of individual component as well as by the chemical reaction running after the instantaneous x_e appropriate to the momentary total amounts of nitrogen and hydrogen elements in contact with the catalyst. Calculation shows however that the shift of x due to the latter cause is quite within the experimental error in the present case of experiment.*) It hence follows from the experimental result, that the leak does not shift x or that every component leaks with the same specific rate, i.e., by the same fraction simultaneously.

On the basis of the conclusion thus arrived at, the rate of increase of ammonia partial pressure is in general expressed as,

$$\frac{d(Px)}{dt} = V_S - kPx \qquad (12.x)$$

and that of the total pressure as,

$$\frac{dP}{dt} = -V_S - kP \qquad (12.P)$$

where V_S has the negative sign on account of the stoichiometric relation (1), that the mol number of the whole gas decrease as much as that of ammonia increases.

Eliminating dP/dt from (12), we have,

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*) The x_e at the initial total pressure 30.6 atm. is calculated at 0.0612 according to (6.e) from $x_e =$ 0.0596 at 29.5 atm. given in Table 6.

Eq. (9.x) is now integrated as,

$$x = x_0 e^{-r_1 t} + \alpha t + \left(x_{e,0} - \frac{\alpha}{r_1} \right) (1 - e^{-r_1 t})$$

assuming x_e the linear function of time as,

$$x_e = x_{e,0} + \alpha t$$

where $x_{e.0} = 0.0612, \quad \alpha = \frac{0.0596 - 0.0612}{240} = -0.67 \times 10^{-5} \text{ min.}^{-1}$

$$x_0 = 0.0600,$$

suffix 0 referring to $t=0$. Putting $r_1 = 2.86 \times 10^{-3} \text{ min.}^{-1}$ according to Table 5, it is concluded from the above expression of x that x increases monotonously from 0.0600 to its final value 0.0601 at $t = 240$ min. The variation of x due to the chemical reaction is hence quite negligible.

TABLE 4. Leakage of Apparatus.
Temperature :— 450°C
Ammonia mol fraction calculated :— 0.060*)

Time t min.	Total Pressure atm.	Ammonia Mol Fraction x
0	30.6	0.0611
30	30.5	0.0605
60	30.3	0.0597
90	30.2	0.0608
120	30.0	——
150	30.0	0.0603
180	29.8	0.0593
210	29.6	0.0602
240	29.5	0.0602

$$P\frac{dx}{dt} = (1+x)\,V_S$$

which shows that (7.x) remains exact even in the presence of leakage. Since the same is true with (6.V), (8) derived from (7.x) and (6.V) must also remain valid. Let t_e be the time at which the equilibrium mol fraction is just at a particular value x_e. The right of (8) is now expanded as the function of x and t around x_e and t_e remembering (7.P) and (11.P) and neglecting higher order terms, as,

$$\dot{x} = -r_1(x-x_e)-r_1r_t(t-t_e) \tag{13.x}$$

where,

$$r_1 = \frac{2}{n}\frac{\vec{\mathfrak{R}}_e}{P_e}\frac{1+3x_e}{x_e(1-x_e)} \tag{13.a}$$

$$r_1r_t = \frac{2}{n}\frac{\vec{\mathfrak{R}}_e}{P_e}(1+x_e)\,k \tag{13.b}$$

Eq. (13.x) may readily be solved as,

$$x-x_e = -r_t\left(t-t_e-\frac{1}{r_1}\right)+C'e^{-r_1(t-t_e)}$$

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*) Calculated from the known amount of ammonia admixed with 1 : 3 gas, the initial total pressure and known volume of the reaction chamber and the communicated space.

or as,

$$\log\left|x-x_e+r_t\left(t-t_e-\frac{1}{r_1}\right)\right| = -r_1t+\text{const} \tag{14.x}$$

where C' is the integration constant and,

$$r_t=\frac{x_e(1-x_e^2)}{1+3x_e}k \tag{14.b}$$

We have on the other hand eliminating V_S from (12),

$$\frac{dP}{P}+\frac{dx}{1+x}=-k\,dt$$

or by integration,

$$P(1+x)=Ce^{-kt}$$

or particularly for P_e, x_e and t_e,

$$P_e(1+x_e)=Ce^{-kt_e} \tag{15}$$

where $\log C$ is the integration constant.

The r_1 and x_e were now adjusted in accordance with simultaneous equations (14.x) and (15) to the observation of each series by means of the method of least squares as below, assigning P_e of (15) the average pressure 29.5 atm. of $\mathfrak{K}_e$-determination described later.

Neglecting first $r_t\left(t-t_e-\dfrac{1}{r_1}\right)$ on the left of (14.x) altogether, x_e and r_1 were provisionally determined by fitting them in with the appropriate linearity graphically.

The corresponding approximate values of r_t and t_e were now determined by (14.b) and (15) respectively substituting in them the above values of x_e, r_1 and P_e, C evaluated for each series at the average over those calculated each from a simultaneous set of P, x and t, and k of (11.k).

Writing now as,

$$\begin{aligned} r_t &= r_t'+\Delta r_t\,, & x_e &= x_e'+\Delta x_e\,,\\ t_e &= t_e'+\Delta t_e\,, & r_1 &= r_1'+\Delta r_1\,. \end{aligned} \tag{16}$$

where prime denote the above obtained approximate values, (14.x) is expanded with respect to increments Δx_e etc. as,

$$\log\left\{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)\right\}-\frac{\Delta x_e}{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)}+\frac{\Delta r_t\left(t-t_e'-\frac{1}{r_1'}\right)}{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)}$$
$$-\frac{r_t'\,\Delta t_e}{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)}+\frac{\frac{r_t'}{(r_1')^2}\,\Delta r_1}{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)}=-r_1't-\Delta r_1t+\text{const}$$

Eliminating Δr_t and Δt_e by virtue of the relations derived from (14.b) and (15),

$$\Delta r_t = k\,\frac{1-3(1+2x_e')\,x_e'^2}{(1+3x_e')^2}\,\Delta x_e$$

$$\Delta t_e = -\,\frac{\Delta x_e}{k\,(1+x_e')}$$

we have,

$$\log\left\{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)\right\}+\frac{1}{x-x_e'+r_t'\left(t-t_e'-\frac{1}{r_1'}\right)}$$

$$\times\left[\left\{-1+k\,\frac{1-3\,(1+2x_e')\,x_e'^2}{(1+3x_e')^2}\left(t-t_e'-\frac{1}{r_1'}\right)+\frac{r_t'}{k\,(1+x_e')}\right\}\Delta x_e\right.$$

$$\left.+\left\{t\,(x-x_e')+r_t't\left(t-t_e'-\frac{1}{r_1'}\right)+\frac{r_t'}{r_1'^2}\right\}\Delta r_1\right] = -r_1't+\text{const}$$

The Δx_e and Δr_1 were now adjusted to the observation according to the above linear equation by the method of least squares, probable values of x_e and r_1 determined by (16), and henceforth those of r_t and t_e of the same degree of approximation according to (14. *b*) and (15).

Substituting now these values of x_e, r_1, r_t and t_e respectively in x_e', r_1', r_t' and t_e' in the above equation, Δx_e, Δr_1 and hence x_e and r_1 of higher approximation were calculated. The successive approximation was carried on until no variation of x_e or r_1 practically resulted.

Table 5 shows the most probable values of r_1 and x_e thus arrived at and associated probable errors of these indirect observations. The x_e in parenthesis were calculated from the empirical equation due to HABER[4],

$$\log K_P = 2098.2/T - 2.509\log T - 1.006\times10^{-4}T + 1.859\times10^{-7}T^2 + 2.10$$

Fig. 2, (b) illustrates the linearlity of (14. x) based on the above data at 450°C. Upper or lower group of points is that of decomposition or of synthesis respectively referred to the ordinate on the right or left shifted from each other to avoid overlapping. Obsevations below 100 min. were excluded from the above calculation, because of a considerable deviation from the linearity expected duly from the neglect of terms higher than the second order in arriving at (13. x).

The reliability of this method of determining of r_1 and x at equilibrium, where (13. x) used holds exactly, is assured, admitted that r_1 varies continuously across the equilibrium point, by the validity of the linear relation close to equilibrium and by the coincidence respectively of r_1- or of x_e-values determined independently from synthesis and decomposition observations. This result is further amplified by the

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[4] HABER, Z. Elek. Chem. 20, 603 (1914).

satisfactory agreement of x_e-data shown in Table 5 with those directly observed by HABER4).

§ 8. $\vec{\mathfrak{R}}_e$-Determination and Stoichiometric Number

The $\vec{\mathfrak{R}}_e$ was determined by means of N^{15}-shifted ammonia by preparing a mixture of 1 : 3 gas and 6.00% ammonia of ca. 4% N^{15}-atomic fraction in R_2 at 44.5 atm. total pressure just as for decomposition series in §5. In the mean time the residual gas in R_1 of r_1-determination*) was purged to atmospheric pressure, the preliminary treatment stated in §5 carried out and the gas purged again to atmospheric pressure. The mixture prepared in R_2 as above was now led into R_1 kept at 450°C to make 30 atm. pressure.

It took about 15 min. after the last purge to introduce the prepared mixture into R_1 and hence more or less ammonia must have been present in the residual gas in R_1. The resultant mol fraction in R_1 is calculated at,

$$\frac{0.002\times 1+0.060\times 29}{30}=0.0581 \quad \text{or} \quad 0.0580$$

according as the residual gas is in equilibrium i. e. of 0.002 ammonia mol fraction in accordance with the previous paper or contains practically no ammonia. The ammonia content in the residual gas in R_1 makes hence very little and the resultant mol fraction is very close to x_e determined in conjunction with r_1 as given in Table 5.

It may similarly be shown that the associated dilution of N^{15}-shift by normal ammonia possibly present in the residual gas is negligibly small.

After 4 to 3 hours when the total pressure decreased down to 29 atm. the content of R_1 was purged from 29 to 27 atm. for 5 minutes through a trap, containing dilute sulphuric acid, fitted to the apparatus in place of A to fix ammonia and to measure its isotopic shift. The remaining gas was further purged down to normal pressure through a trap cooled by liquid air now fitted to the apparatus in place of the above trap for recovering the N^{15}-shifted ammonia. After the usual preliminary treatment mentioned in §5, the similar experiment was repeated in succession. The second and third $\vec{\mathfrak{R}}_e$-measurements were carried out just similarly using each a fresh portion of shifted ammonia and the fourth one with the remaining fresh portion of the sample added with recovered ones of foregoing three determinations.

The isotopic analysis of ammonium sulphate sample was conducted by Dr. A. SUGIMOTO of the Scientific Research Institute, Ltd. Tokio by means of mass spectrometer.

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*) That of Series II (Decomposition). Cf. § 5.

The results of the experiments at 450°C and 30~29 atm. are shown in Table 6.

Allowing for the leakage, an expression of $\vec{\mathfrak{R}}_e$,

$$\vec{\mathfrak{R}}_e = P_e^{\mathrm{NH}_3} \frac{2P_0^{\mathrm{N}_2}}{P_0^{\mathrm{NH}_3} + 2P_0^{\mathrm{N}_2}} \frac{1}{t} \log \frac{Z_0^{\mathrm{NH}_3} - Z_\infty^{\mathrm{NH}_3}}{Z^{\mathrm{NH}_3} - Z_\infty^{\mathrm{NH}_3}} \tag{17}$$

was derived as below, where suffix 0 denoted quantities at $t=0$, Z^{NH_3} the atomc fraction of N^{15} in ammonia and $Z_\infty^{\mathrm{NH}_3}$ that averaged over ammonia and nitrogen at $t=0$, i.e.

$$Z_\infty^{\mathrm{NH}_3} = \frac{P_0^{\mathrm{NH}_3} Z_0^{\mathrm{NH}_3} + 2P_0^{\mathrm{N}_2} Z_0^{\mathrm{N}_2}}{P_0^{\mathrm{NH}_3} + 2P_0^{\mathrm{N}_2}} \tag{18}$$

The total amount of N^{15} in ammonia is given by $P^{\mathrm{NH}_3} \times Z^{\mathrm{NH}_3}$ and its rate of decrease by $-\frac{d}{dt}(P^{\mathrm{NH}_3} Z^{\mathrm{NH}_3})$. Expressing the same quantity alternatively by $\overleftarrow{\mathfrak{R}} Z^{\mathrm{NH}_3} + kP^{\mathrm{NH}_3} Z^{\mathrm{NH}_3} - \vec{\mathfrak{R}} Z^{\mathrm{N}_2}$, where $\vec{\mathfrak{R}}$ or $\overleftarrow{\mathfrak{R}}$ is the forward or backward rate of ammonia synthesis and $kP^{\mathrm{NH}_3} Z^{\mathrm{NH}_3}$ the loss by leakage, we have,

$$-\frac{d}{dt}(P^{\mathrm{NH}_3} Z^{\mathrm{NH}_3}) = \overleftarrow{\mathfrak{R}} Z^{\mathrm{NH}_3} + kP^{\mathrm{NH}_3} Z^{\mathrm{NH}_3} - \vec{\mathfrak{R}} Z^{\mathrm{N}_2}$$

or, according to (12. x), (5. NH_3) and to the relation, $\vec{\mathfrak{R}} - \overleftarrow{\mathfrak{R}} = V_S$ which follows from the definition,

$$\frac{dZ^{\mathrm{NH}_3}}{dt} = \frac{\vec{\mathfrak{R}}}{P^{\mathrm{NH}_3}} (Z^{\mathrm{N}_2} - Z^{\mathrm{NH}_3}) \tag{19}$$

It follows on the other hand from the common specific rate of leakage to every components*), that the total amount q of N^{15} in the reaction chamber decreases as,

$$-\frac{1}{q}\frac{dq}{dt} = k$$

or as,

$$q = q_0 e^{-kt}$$

and partial pressures of ammonia and nitrogen do similarly as,

$$P^{\mathrm{NH}_3} = P_0^{\mathrm{NH}_3} e^{-kt}, \qquad P^{\mathrm{N}_2} = P_0^{\mathrm{N}_2} e^{-kt}$$

Writing now q as,

$$q = P^{\mathrm{NH}_3} Z^{\mathrm{NH}_3} + 2P^{\mathrm{N}_2} Z^{\mathrm{N}_2}$$

we have from above four equations,

$$P_0^{\mathrm{NH}_3} Z^{\mathrm{NH}_3} + 2P_0^{\mathrm{N}_2} Z^{\mathrm{N}_2} = P_0^{\mathrm{NH}_3} Z_0^{\mathrm{NH}_3} + 2P_0^{\mathrm{N}_2} Z_0^{\mathrm{N}_2} \tag{20}$$

noting that q_0 is expressed in the right of the above equation.

Eliminating now Z^{N_2} from (19) and (20) remembering (18), we have,

$$\frac{dZ^{\mathrm{NH}_3}}{dt} = \frac{\vec{\mathfrak{R}}}{P^{\mathrm{NH}_3}} \left(\frac{P_0^{\mathrm{NH}_3}}{2P_0^{\mathrm{N}_2}} + 1 \right) (Z_\infty^{\mathrm{NH}_3} - Z^{\mathrm{NH}_3}) \tag{21}$$

or by integration,

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*) Cf. §7.

$$\log \frac{Z_0^{NH_3} - Z_\infty^{NH_3}}{Z^{NH_3} - Z_\infty^{NH_3}} = \overline{(\vec{\mathfrak{R}}/P^{NH_3})}\, t \left(\frac{P_0^{NH_3}}{2P_0^{N_2}} + 1 \right)$$

where,

$$\overline{(\vec{\mathfrak{R}}/P^{NH_3})} = \frac{1}{t} \int_0^t \frac{\vec{\mathfrak{R}}}{P^{NH_3}}\, dt$$

is the time mean of $\vec{\mathfrak{R}}/P^{NH_3}$ over the period of experiment. The $\vec{\mathfrak{R}}/P^{NH_3}$ should however equal $\vec{\mathfrak{R}}_e/P_e{}^{NH_3}$ at the mean total pressure 29.5 atm., inasmuch as the present experiment was conducted with the equilibrium gas mixture at that total pressure. We might identify its time mean $\overline{(\vec{\mathfrak{R}}/P^{NH_3})}$ with $\vec{\mathfrak{R}}_e/P_e^{NH_3}$ i. e. $\vec{\mathfrak{R}}/P^{NH_3}$ at the mean total pressure and express $\vec{\mathfrak{R}}_e$ as in (17).

§ 9. Stoichiometric Number of The Rate-determining Step

The stoichiometric number n of the rate-determining step is now determined as shown in Table 6 according to (13.a) and (17) from the result given in Table 5 and 6. Initial partial pressure of ammonia and nitrogen in (17) were calculated according to (5) from the initial total pressure 30 atm. and the initial mol fraction 0.058 of ammonia. The r_1 or x_e used for the calculation is the weighted mean of those of synthesis and decomposition at 450°C given in Table 5. The $Z_\infty^{NH_3}$ of (18) was calculated from the initial partial pressures, $Z_0^{NH_3}$, and $Z_0^{N_2}$ identified with the natural abundance 0.38% of N^{15}.

TABLE 5. r_1 and x_e Values.

Temperature		450°C	475°C	492°C
r_1 (min.$^{-1}$ × 10^3)	Synthesis	2.85 ± 0.14	10.30 ± 0.65	18.9 ± 3.0
	Decompos.	2.94 ± 0.64	9.86 ± 0.25	17.3 ± 4.0
x_e (Mol. Fraction)	Synthesis	0.0597 ± 0.0006	0.0472 ± 0.0007	0.0379 ± 0.0008
	Decompos.	0.0572 ± 0.0024	0.0468 ± 0.0003	0.0387 ± 0.0009
	(HABER)	(0.0606)	(0.0452)	(0.0385)

The last column of Table 6 shows the stoichiometric number n thus calculated with probable error derived from those of basic data. The weighted mean of n is 1.86±0.10. It may be concluded from this result that the stoichiometric number of the rate-determining step of the catalysed ammonia synthesis is 2 or the rate-determining step is one of last three steps of (2) at 29.5 atm. and 450°C similarly as in the previous case of ordinary pressure, provided that the genuine chemical reaction at the catalyst's surface controls the observed change, that reaction (1) and its reversal are exclusively responsible for the observed isotopic replacement and that reaction (1) consists solely in the sequence of steps (2).

TABLE 6. Observed Shift Z of N^{15} and Stoichiometric Number n of The Rate-Determining Step.

Temperature :— 450°C
Total pressure :— 30∼29 atm.
r_1 :— $(2.86 \pm 0.14)\ \text{min}^{-1} \times 10^{-3}$*) x_e :— (0.0596 ± 0.0006)*)

$Z_0^{NH_3}$ (%)	Z^{NH_3} (%)	$Z_\infty^{NH_3}$ (%)	t (min.)	n
3.74 ± 0.01	2.56 ± 0.02	0.765 ± 0.001	240	1.58 ± 0.17
3.50 ± 0.03	2.08 ± 0.04	0.738 ± 0.002	240	2.25 ± 0.23
4.31 ± 0.02	3.14 ± 0.01	0.829 ± 0.002	180	1.70 ± 0.18
4.44 ± 0.02	2.94 ± 0.03	0.844 ± 0.002	180	2.24 ± 0.23

It may be shown that $\log r_1$ in Table 5 runs fairly linearly with the reciprocal absolute temperature, the appropriate inclination $\frac{d \log r_1}{d(1/RT)}$ amounting to 48 Kcal, from which it is similarly concluded as in the previous paper[1]) that the observed change is controlled by the genuine chemical reaction at the catalyst's surface at least at the lowest temperature of observation, 450°C.

If any other reaction contributes to the isotopic replacement concurrently with the synthesis reaction, observed $\mathfrak{R}_e$ must be shared by the other one and hence the true stoichiometric number of ammonia synthesis must be in accordance with (9.1) less than 2. Only possible case would then be that when $n=1$ for the synthesis or that of equal contributions from both the reactions to the isotopic replacement.

Excluding such an extremely improbable case, similarly as in the previous paper[1]), our conclusion is that the rate-determining step is one of those,

$$\begin{aligned} N(a) + H(a) &\longrightarrow NH(a) \\ NH(a) + H(a) &\longrightarrow NH_2(a) \\ NH_2(a) + H(a) &\longrightarrow NH_3 \end{aligned}$$

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*) Weighted mean of r_1 or x_e of synthsis and decomposition given in Table 5·

even at 29.5 atm. total pressure, provided that sequence (2) is solely responsible for the ammonia synthesis.

Summary

Stoichiometric number of the rate-determining step to the catalysed ammonia synthesis,

$$N_2 + 3H_2 = 2NH_3$$

in the presence of the doubly promoted commercial synthesis catalyst at 450°C and 29.5 atm. pressure was determined by measuring statically the reaction rate in the neighbourhood of equilibrium as well as its forward rate by means of N^{15} on the basis of the general theory of the stoichiometric number. The observation was corrected for slight leak of gas from the apparatus used. The stoichiometric number of the rate-determining step was found 2, i.e., the rate-determining step occurs twice every overall reaction expressed as above. It was concluded from the result that the rate-determining step was one of last three steps of the sequence,

$$H_2 \longrightarrow 2H(a)$$
$$N_2 \longrightarrow 2N(a)$$
$$N(a) + H(a) \longrightarrow NH(a)$$
$$NH(a) + H(a) \longrightarrow NH_2(a)$$
$$NH_2(a) + H(a) \longrightarrow NH_3$$

provided that the reaction followed the sequence at all.

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