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THE MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST I: OBSERVATION OF THE DECOMPOSITION RATE

By

Juro HORIUTI and Isamu TOYOSHIMA^{*)}

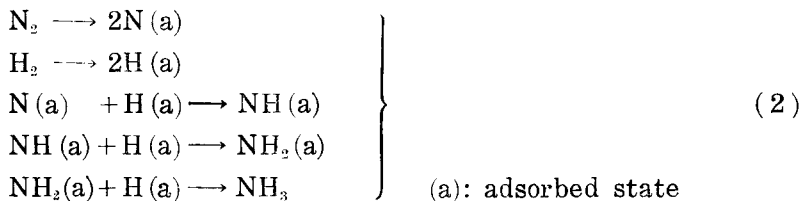
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Introduction

ENOMOTO, KOBAYASHI and one of the present authors¹⁾²⁾ have found the stoichiometric number^{**)3)} 2 of the rate-determining step of the catalyzed ammonia synthetic reaction



in the presence of doubly promoted iron catalyst at ordinary¹⁾ as well as 29.5 atm²⁾ pressure. This conclusion confines the part of determining the rate to one of the last three steps of the sequence



provided that the catalyzed synthesis follows the sequence (2) at all^{**)3)}.

It is the purpose of the present work to identify the rate-determining step in extension of above results from the kinetic analysis of the catalyzed decomposition of ammonia in the presence of the same catalyst. It is well-known, that iron of the catalyst forms different nitrides in the presence of ammonia, which exists of course more or

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^{**)3)} The stoichiometric number is the number of times of a step to occur for every overall reaction defined by a definite chemical equation; those of the first, second and the last three steps of the sequence (2) are thus 1, 3 and 2 respectively with reference to the overall reaction (1).

less in excess in the case of catalyzed decomposition. The iron-ammonia-hydrogen system has been exhaustively investigated by EMMETT and collaborators⁴⁾ and a number of other authors⁵⁾ with consistent results, which assures, in particular, that catalyst iron used by ENOMOTO, HORIUTI and KOBAYASHI^{1,2)} forms α -phase, i.e. solid solution of nitrogen in iron.

The present experiment has been carried out, securing the same state of the catalyst, by flowing the catalyst's bed steadily with 1:4 ammonia-hydrogen mixture at 1 atm total pressure and 450–540°C, and the outflow rate of ammonia was observed for determining the rate of ammonia decomposition as the function of temperature and the composition of gas mixture as detailed below. The analysis of the results for the rate-determining step will be reported in a subsequent paper.

§ 1. Materials

Catalyst used is a different portion of the same preparation as that used by ENOMOTO, HORIUTI and KOBAYASHI^{1,2)}, i.e. doubly promoted iron catalyst containing 1.82% Al_2O_3 , 1.06% K_2O , 0.41% SiO_2 , 0.04% CaO and a trace of MgO .

Cylinder hydrogen was passed over reduced copper gauze and then nickel gauze respectively of 39 and 31 cm³ apparent volumes both kept at 600°C, four columns of silica gel each of 4 cm diameter and 40 cm length successively and then over phosphorous pentoxide. Hydrogen thus purified was used for the decomposition experiment as well as for the reduction of catalyst.

Cylinder ammonia was dried over soda lime and solid potassium hydroxide before use.

§ 2. Apparatus

The apparatus for the decomposition experiment is shown in Fig. 1. R is the quartz reaction chamber of 75 cm length and 3.4 cm inner diameter containing 100.7 gm (before reduction) catalyst in a 6 cm high bed resting between layers of Raschig rings supported by glass wool packed above and beneath. The electric furnace F_1 keeps the catalyst's bed at a desired temperature and preheats inflow gas. J_1 , J_2 , J_3 and J_4 are four alumel-chromel thermojunctions held respectively at the top, middle, bottom on the axis and on the wall at the middle height

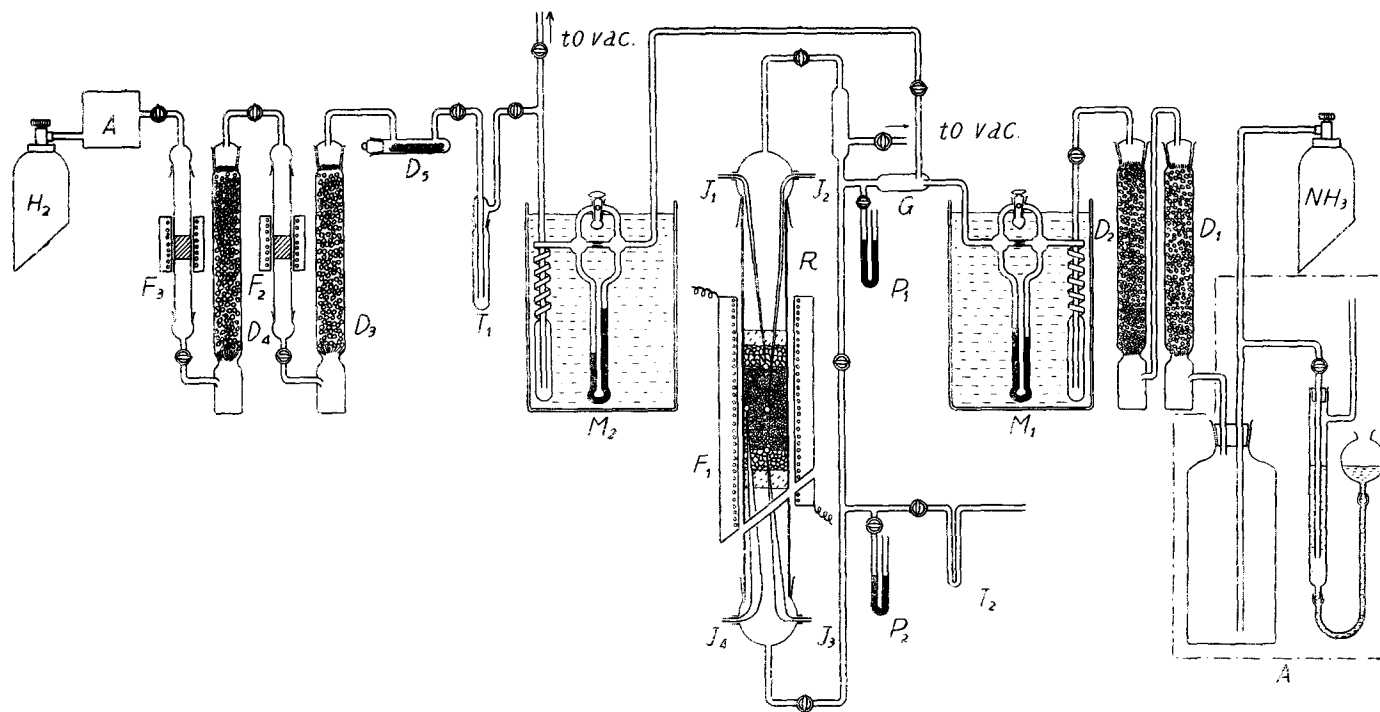


Fig. 1 Apparatus

- | | | | |
|--------------|----------------------------------|--------------|--|
| R | : Reaction chamber | F_1 etc.: | Electric furnaces (F_2 or F_3 for Ni or Cu gauze) |
| M_1, M_2 : | Flow meters | A | : Pressure regulator (gas overflow) |
| D_1 | : Soda lime | D_2 | : Potassium hydroxide |
| D_3, D_4 : | Silica gel (each in two columns) | D_5 | : Phosphorous pentoxide |
| J_1 etc.: | Thermojunctions | P_1, P_2 : | Manometers |
| T_1, T_2 : | Traps | | |

The Mechanism of Catalyzed Decomposition of Ammonia

respectively of the catalyst bed, J_1 being automatically kept at the desired temperature by means of a potentiometric thermoregulator within $\pm 2^\circ\text{C}$; J_1 etc. were calibrated at melting points of tin, lead, zinc and antimony. M_1 and M_2 are flowmeters, shown schematically, for ammonia and hydrogen respectively; each of them is a multicapillary arrangement thermostated at 25°C covering a range of flow rate from 20 to 2000 cc/min with $\pm 0.4\%$ probable errors; after being thus measured individually of the flow rate, ammonia and hydrogen are mixed at G, before flown through the catalyst's bed. P_1 and P_2 are manometers, A is the gas overflow for keeping the gas pressure constant and D_1 etc. are towers of drying agents mentioned in the foregoing section.

§ 3. Procedure of Experiment

The bed of reduced catalyst kept at a definite temperature by J_1 as described above is flown with 1 : 4 ammonia-hydrogen mixture and the constant outflow rate N'_A of ammonia finally attained is determined for each run of fixed catalyst's temperature and fixed inflow rate of gas mixture. Runs of different catalyst's temperatures and inflow rates are conducted successively with one and the same portion of the catalyst throughout as below.

The bed of catalyst before reduction is set in R as described in § 2 and reduced *in situ* in 100 cc/min hydrogen stream for 110 hours at 400°C , then for 160 hours at 500°C and finally for 300 hours at 600°C until the condensation of water in outflow gas is imperceptible in a trap in liquid nitrogen.

The catalyst reduced as above is now subjected to the preliminary treatment of flowing it with hydrogen at 550°C for 4 to 5 hours and then at the temperature of the run going to be conducted for half or an hour. The run is now started just by switching the hydrogen stream to that of 1 : 4 ammonia-hydrogen mixture of constant flow rate. The outflow rate of ammonia is now repeatedly observed until it attains a constant value at respectively fixed catalyst's temperature and inflow rate.

Three to five runs were carried out in succession in the course of a day, the catalyst being subjected to the preliminary treatment described above before and after the daily work, as well as before changing the temperature of the run in course of a day. On closing the daily work, the catalyst's bed was cooled in pure hydrogen flow

TABLE 1. Experimental results.

$$N_H/N_A = 4.00 \pm 0.023$$

No. of Runs ^{*)}	Date 1952	Temperature °C					Inflow rate of		Ammonia outflow rate $N_{A'}$ mol/min $\times 10^3$	Fraction of ammonia outflow rate $y_e^A = \frac{N_{A'}}{2N_A - N_{A'} + N_H}$	Remarks
		t_1	t_2	t_3	t_4	Average	NH ₃ , N_A mol/min $\times 10^3$	H ₂ , N_H mol/min $\times 10^3$			
1	July 6	472	471	472	484	475	0.902	3.625	0.446	0.090	
2	"	472	472	474	484	476	1.786	7.188	1.135	0.118	
3	"	472	470	474	485	475	4.464	17.86	3.535	0.150	
4	7	472	471	471	484	475	2.781	10.98	1.863	0.126	
5	"	467	468	478	488	475	8.929	35.71	7.842	0.172	
6	"	472	470	472	484	476	1.107	4.451	0.581	0.096	
33	21	472	469	486	484	474	2.746	10.98	1.925	0.133	Probable error of y_e^A : 1.2%
34	"	460	463	486	484	476	18.08	72.54	16.81	0.183	
37	Oct. 30	472	472	472	481	474	3.180	12.41	2.222	0.135	Several Runs at N_H/N_A =10 and 487°C or 474 °C inserted between Runs 36 and 37
7	July 8	447	447	447	457	450	0.911	3.692	0.710	0.149	
8	"	447	447	450	460	451	1.263	5.022	1.005	0.153	
9	"	447	447	450	458	450	2.746	16.16	2.377	0.168	
10	9	447	447	448	460	451	1.786	7.188	1.474	0.159	Probable error of y_e^A : 1.1%
11	"	447	447	450	462	451	4.464	17.85	4.013	0.176	
35	22	445	445	450	462	450	8.929	35.71	8.558	0.190	Probable error of y_e^A : 1.8%
12	July 13	485	484	484	496	487	0.902	3.549	0.252	0.049	
13	"	485	484	484	496	487	1.263	5.045	0.451	0.063	

14	July	13	486	484	484	496	487	1.786	7.188	0.768	0.077
15		"	485	484	485	496	488	4.464	17.85	2.843	0.121
16		14	485	482	484	496	488	2.746	10.98	1.468	0.098
17		"	484	483	486	496	487	8.973	35.71	6.828	0.145
18		"	480	479	489	501	487	18.08	72.54	16.21	0.176
19	July	15	509	505	509	521	511	0.911	3.661	0.052	0.010
20		"	509	505	509	521	512	1.263	5.044	0.185	0.018
21		"	510	506	509	521	512	1.786	7.188	0.209	0.020
22		"	511	506	509	521	512	4.487	17.95	1.528	0.060
23		16	502	501	516	530	512	18.04	72.54	13.71	0.145
24		"	509	504	511	521	513	8.973	35.71	5.450	0.113
25		"	510	506	509	521	512	2.746	10.98	0.507	0.032
26		17	509	506	509	521	511	6.696	26.88	3.363	0.090
27		"	509	504	509	521	511	1.339	5.357	0.122	0.015
36		23	509	506	509	521	511	4.464	17.95	1.533	0.061
28	July	18	530	526	530	542	532	2.679	10.98	0.151	0.010
29		"	533	526	530	542	533	4.531	18.08	0.631	0.024
30		"	531	524	530	546	533	3.929	35.71	3.389	0.068
31		"	526	520	533	548	532	18.04	72.54	10.43	0.107
32		"	530	526	530	542	532	1.786	7.188	0.056	0.005

*) Runs have been conducted in the order of their numbers, those of approximately the same averaged temperatures being grouped together in the Table.

down to 200°C after the above treatment, shut off by stopcocks and left overnight at the same temperature in hydrogen atmosphere. Fairly reproducible results were obtained by this procedure.

The outflow rate N'_A of undecomposed ammonia was determined by passing it through sulphuric acid solution of known concentration for a recorded time and by titrating it back.

§ 4. Experimental Results

The experimental results are shown in Table 1. The temperature readings t_1 , t_2 and t_3 respectively of thermojunctions, J_1 , J_2 and J_3 on the axis are coincident with each other within a few degrees in most of runs except in those at higher temperatures and higher inflow rates, whereas that t_4 of J_4 on the wall is considerably higher than the formers. Ammonia outflow rate N'_A given in the Table is the average of several measurements for each run, probable errors of them being 1% except in cases when otherwise remarked.

Fraction y_e^A of ammonia outflow rate over the total outflow rate in the second last column is given as

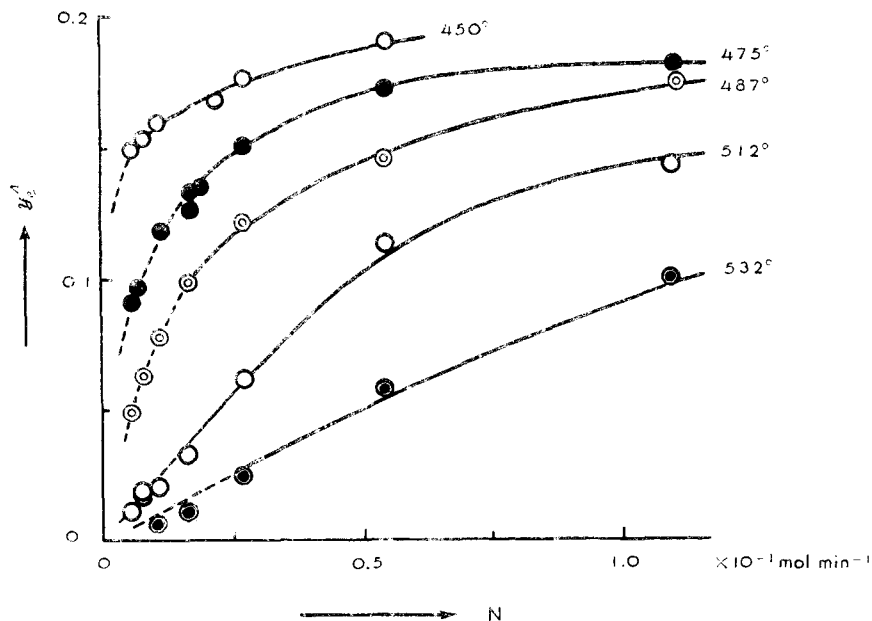


Fig. 2 Fraction y_e^A of ammonia outflow rate vs. $N=2N_A+N_H$
 N_A , N_H : ammonia or hydrogen inflow rate. Temperature
 designated: mean of "Averages" of each group in Table 1.

$$y_e^A = \frac{N_A'}{2N_A - N_A' + N_H}, \quad (3)$$

where N_A or N_H is the ammonia or hydrogen inflow rate and the denominator is twice the decrease $N_A - N_A'$ of ammonia flow rate, giving the total increment of nitrogen and hydrogen flow rates, plus N_A' and N_H . Fig. 2 shows the plots of y_e^A vs. $N = 2N_A + N_H$.

§ 5. Determination of the Decomposition Rate

Results of observation given in Table 1 were analyzed for the decomposition rate U of ammonia, i.e. the number of mols of ammonia decomposed per min per cc of the catalyst's bed at different temperatures and compositions of the gas mixture; U is first expressed by observed quantities under idealized conditions given below, and corrected for deviations from the idealizations as described in later sections, admitting U as a function of temperature and mol fraction x^A of ammonia.

(I) The flow of gas components and the conversion among them proceed steadily throughout.

(II) The flow rate and the mol fraction x^δ of every gas component δ are respectively homogeneous over every horizontal section of R throughout, where δ represents ammonia, nitrogen and hydrogen denoted in what follows respectively by A, N and H.

(III) The x^δ of any gas component δ equals everywhere the fraction y^δ of its flow rate.

(IV) Temperature is homogeneous throughout R.

From (I) we have immediately

$$2n^N + n^A = N_A', \quad n^H = 3n^N + N_H, \quad (4. A), (4. H)$$

where n^δ is the flow rate of δ , since one half the decrease $N_A - n^A$ of ammonia flow rate, n^N , and one third the increase $n^H - N_H$ of hydrogen flow rate should equal each other by the stoichiometric relation (1). Expressing the fraction y^A of ammonia flow rate as

$$y^A = n^A / (n^A + n^N + n^H), \quad (5. y)$$

we have, eliminating n^N and n^H from the above three equations,

$$n^A = \frac{y^A}{1 + y^A} N, \quad (5. A)$$

where

$$N = 2N_A + N_H. \quad (5. N)$$

It is deduced from (II) and (IV), on the other hand, that U is homogeneous over every horizontal section. The decrease $-dn^A$ of ammonia flow rate between two horizontal sections of S area at dh distance equals now $USdh$ according to (I), i.e.

$$-dn^A = USdh, \quad (6. n)$$

h being the depth of a horizontal section measured from the top of the catalyst's bed downwards. We have hence according to (5.A)

$$-\frac{Ndy^A}{(1+y^A)^2} = SUdh, \quad (6. y)$$

or by integration

$$-\int_{y_i^A}^{y_e^A} \frac{dy^A}{U(1+y^A)^2} = \frac{V}{N}, \quad (7)$$

where V is the volume of the catalyst's bed and suffix i or e signifies quantities at the inlet or exit of the catalyst's bed respectively, as in what follows. Differentiating (7) with respect to $1/N$, we have

$$U_e = -\frac{dy_e^A/d(1/N)}{V(1+y_e^A)^2}, \quad (8)$$

since U is a function solely of y^A in accordance with (III) and (IV); (8) determines U in terms of U_e as the function of x^A , identical with y_e^A , and temperature t of the relevant run under the above idealized conditions.

§ 6. Deviation from the Idealizations

Among the idealized conditions, (I) will be taken sufficiently assured on the ground of appreciably constant N_A observed for any constant N_A and N_H . Allowing now for deviations from (II), (III) and (IV), noting that (7) holds generally for U averaged over the relevant horizontal section, the differentiation provides instead of (8),

$$-\frac{1}{U_e(1+y_e^A)^2} \frac{dy_e^A}{d(1/N)} + [x] + [t] = V, \quad (9. U)$$

where

$$[x] = \int_{y_i^A}^{y_e^A} \frac{dy^A}{U^2(1+y^A)^2} \left(\frac{\partial U}{\partial x^A} \right)_{t_m} \left(\frac{\partial x^A}{\partial (1/N)} \right)_{y^A}, \quad (9. x)$$

$$[t] = \int_{y^A}^{y^c} \frac{dy^A}{U^2(1+y^A)^2} \left(\frac{\partial U}{\partial t_m} \right)_{x^A} \left(\frac{\partial t_m}{\partial (1/N)} \right)_{y^A}. \quad (9. t)$$

U , y^A and x^A are respective averages over the appropriate horizontal section and t_m is such a value of t as just to give the averaged value of U , when put into the original function of $U(t, x^A)$ together with the average x^A .

New assumptions are now introduced in place of (II), (III) and (IV), that the interrelation between x^A and y^A , now representing the respective average values, is identical with that between respectively homogeneous x^A and y^A , and that t_m is determined as in §11.

We now proceed to evaluate $[x]$ and $[t]$ in subsequent sections.

§ 7. Relation between x^δ and y^δ

We investigate the relation between x^δ and y^δ qualitatively before evaluating $[x]$.

The x^δ must of course equal y^δ , if every layer of gas mixture is moving downwards without any mix-up or mass interchange between the layers. Any deviation of x^δ from y^δ should hence be attributed to the mix-up, which is effected by thermal diffusion of gas components as well as by turbulence in gas caused especially by flowing through catalyst grains.

The mix-up gives rise to the additional rate, $-D^\delta CS \partial x^\delta / \partial h$, of flow, where C or S is the total concentration of the gas mixture or the area of horizontal section of R, which are respectively kept constant at the present experimental condition. D^δ is the proportionality constant depending on the extent of the mix-up, or the additional rate across unit area at unit descent, $-C \partial x^\delta / \partial h$, of δ concentration, and is nothing but the diffusion constant, if the mix-up is effected solely by the thermal motion. The resultant flow rate n^δ is now given as

$$n^\delta = -CSD^\delta \frac{\partial x^\delta}{\partial h} + \omega x^\delta, \quad (10)$$

from which we have for the rate ω of mass flow

$$\omega = n + CS \sum D^\delta \frac{\partial x^\delta}{\partial h}, \quad (11. \omega)$$

where

$$n \equiv \sum n^\delta \equiv n^A + n^N + n^H. \quad (11. n)$$

We have from the definition of y^δ , (10) and (11. ω)

$$y^\delta \equiv n^\delta/n = x^\delta - CS/n \cdot (D^\delta \partial x^\delta / \partial h - x^\delta \sum D^\delta \partial x^\delta / \partial h). \quad (12)$$

It has been shown by KANEKO⁶⁾ and POLISSAR⁷⁾ independently, that D^δ due to different kinds of random zig-zag motions, $1, 2, \dots, i, \dots, I$, of constituent particles is given as

$$D^\delta = \frac{1}{6} \sum_{i=1}^I \nu_i^\delta (l_i^\delta)^2, \quad (13)$$

where l_i^δ is the length of the segment of a single rectilinear motion of i -th kind and ν_i^δ its frequency. We assume now that each molecule of our gas mixture is conducting two classes of such sort of motions, i.e. those of thermal motion and of turbulence superposed with each other in accordance with (13). Dividing thus the summation of (13) for the two classes, we have

$$D^\delta = \frac{1}{6} \sum_t \nu_t^\delta (l_t^\delta)^2 + \frac{1}{6} \sum_p \nu_p^\delta (l_p^\delta)^2, \quad (14)$$

where t or p numbers the terms in (14) respectively appropriate to the thermal motion or to the turbulence.

The thermal part is transformed as shown by KANEKO⁶⁾, with special reference to gaseous molecules, as

$$\sum_t \nu_t^\delta (l_t^\delta)^2 = 2\bar{v}_t^\delta \lambda_t^\delta,$$

where \bar{v}_t^δ is the mean velocity of δ and λ_t^δ the mean free path in accordance with the gas kinetic theory. Assuming that the similar transformation is valid to the summation $\sum_p \nu_p^\delta (l_p^\delta)^2$, we have from (14)

$$D^\delta = \frac{1}{3} (\bar{v}_t^\delta \lambda_t^\delta + \bar{v}_p^\delta \lambda_p^\delta), \quad (15)$$

where \bar{v}_p^δ or λ_p^δ is the relevant mean velocity or mean free path respectively corresponding to \bar{v}_t^δ or λ_t^δ .

The λ_t^A , λ_t^N and λ_t^H are respectively determined at 5.92×10^{-6} , 8.5×10^{-6} , 16.0×10^{-6} cm in the respective pure gases at 0°C and 1 atm pressure^{*)}, from which we have $\lambda_t^A \bar{v}_t^A = 1.5$, $\lambda_t^N \bar{v}_t^N = 1.9$ and $\lambda_t^H \bar{v}_t^H = 13 \text{ cm}^2 \text{ sec}^{-1}$ in the respective pure gases at 500°C and 1 atm, assuming λ_t^δ inversely proportional to the concentration and \bar{v}^δ given as $\bar{v}^\delta = \sqrt{8kT/\pi m^\delta}$, where k is the Boltzmann's constant and m^δ the mass of the molecule δ . The

*) Smithsonian Physical Tables, Washington, D. C. 1933.

$\lambda_p^\delta \bar{v}_p^\delta$ is estimated on the other hand at $1 \text{ cm}^2 \text{ sec}^{-1}$ at most, identifying λ_p^δ with the average diameter 0.5 cm of the catalyst's grains and \bar{v}_p^δ with the linear velocity of the gas flow, i.e. 2 cm sec^{-1} at most.

The values $\lambda_i^\delta \bar{v}_i^\delta$ in gas mixture of the present experiment being respectively around the above values of pure gas at 500°C as calculated in later sections, D^δ is, according to (15), practically of the magnitude of the thermal part.

It has, moreover, turned out by actual calculations, that the correction of U for the mix-up effect is as a whole negligibly small at large inflow rate, when the turbulence part of D^δ is significant compared with the thermal part, but that the part is quite insignificant at smaller inflow rate, when the correction for the mix-up effect is as a whole appreciable. It hence follows that the uncertainty, if any, of the above assumptions on the turbulence part affects hardly numerically the corrected result of U .

§ 8. Variation of y^δ with h

We might now qualitatively follow the variation of y^δ with h .

We have for y^A , in particular, from (5. A)

$$y^A = n^A / (N - n^A), \quad (16. A)$$

and similarly for y^N and y^H from (12), (11. n) and (4)

$$y^N = \frac{n^N}{2n^N + N_H + N_A}, \quad y^H = \frac{3n^H}{2n^H + N + N_A}, \quad (16. N), (16. H)$$

or by differentiation

$$\frac{dy^A}{dh} = \frac{N}{(N - n^A)^2} \frac{dn^A}{dh}, \quad (17. A)$$

$$\frac{dy^N}{dh} = \frac{N_H + N_A}{(2n^N + N_H + N_A)^2} \frac{dn^N}{dh}, \quad \frac{dy^H}{dh} = \frac{3(N + N_A)}{(2n^H + N + N_A)^2} \frac{dn^H}{dh}.$$

$$(17. N), (17. H)$$

As coefficients of dn^δ/dh in (17) are all positive and finite*, dy^δ/dh and dn^δ/dh have the same sign and the discontinuity, if any, at the same h . The variation of y^δ may hence be reproduced qualitatively in this regard by that of n^δ .

Fig. 3 shows the variation of n^δ deduced as follows. According to (6. n), n^A varies continuously with h with finite differential coefficient

*) $N - n^A$ in (17. A) is positive and finite according to (4. A) and (5. N)

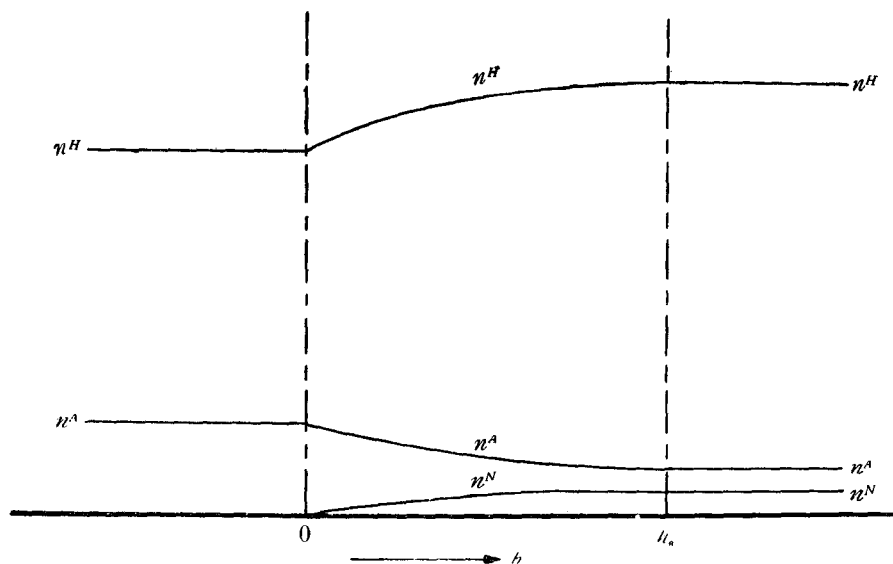


Fig. 3 Variation of flow rate n^δ of component δ with depth h in catalyst's bed.

—US. The same is true with n^N and n^H , as follows from the stoichiometric relation derived from (4), i. e.

$$-dn^A = 2dn^N = \frac{2}{3} dn^H. \quad (18)$$

The flow rate n^δ of every component should be constant before entering the catalyst's bed, i. e. over the region of negative h in accordance with the steady state condition (I). Inside the catalyst's bed, n^A must decrease with increasing h according to (6.n), while n^N or n^H increases respectively monotonously in accordance with (18), perhaps rapidly at first and more and more slowly later along with the decrease of the reactant A.

The $\partial n^\delta / \partial h$ is discontinuous at the inlet or the exit of the catalyst's bed, i. e. at $h=0$ or h_e respectively, as seen from (6.n) and (18), because of positive finite or zero U respectively inside or outside the catalyst's bed. The n^δ are again respectively constant after having left the catalyst's bed similarly as before entering.

§ 9. Variation of x^A with h

We now consider the variation of x^δ with h qualitatively with

reference to that of y^δ deduced in the forgoing section.

In the extreme case, when $CSD^\delta \partial x^\delta / \partial h$ in (10) is negligible, we have by (11.n) and (12)

$$x^\delta = y^\delta, \quad (19)$$

noting

$$\sum x^\delta = 1, \quad (20)$$

by definition.

For the general case it is to be noted, that $\partial x^\delta / \partial h$ must be everywhere continuous at the steady state in distinction from $\partial y^\delta / \partial h$, since otherwise δ must accumulate at or dissipate from the point of the discontinuity of $\partial x^\delta / \partial h$ at an infinite rate, which is hardly counter-balanced for the steady state, by any other process, i.e. gas flow or chemical conversion of finite rate*).

It is now shown as below that x^δ is constant and equals y^δ over the region, $h > h_e$, i.e.

$$x^\delta = y^\delta = \text{const.}, \quad h > h_e. \quad (21)$$

We have from (10) and (12)

$$\frac{y^A + C'D^A \partial x^A / \partial h}{x^A} = \frac{y^N + C'D^N \partial x^N / \partial h}{x^N} = \frac{y^H + C'D^H \partial x^H / \partial h}{x^H}, \quad (22. y)$$

where

$$C' = CS/n. \quad (22. C)$$

It follows, on the other hand, from the relation

$$\partial x^A / \partial h + \partial x^N / \partial h + \partial x^H / \partial h = 0, \quad (23)$$

derived from (20), that there exists positive as well as negative $\partial x^\delta / \partial h$, unless all $\partial x^\delta / \partial h$ simultaneously vanish. In the latter case, we have simply (21) from (20) and (22. y), noting constant y^δ in this region. In the former case, we have the greatest positive $C'D^\delta / x^\delta \times$

*) This statement is exact, if the spaces above and beneath the catalyst's bed in R were packed with such catalytically inactive grains, as providing the same turbulence and hence the same \bar{D}^δ as well as the same effective sectional area to the gas flow as those of the catalyst. These spaces are actually packed by catalytically inactive Raschig rings as stated in §3 in the present experiment, but strictly speaking, the above conditions are not necessarily satisfied. The continuity exists, for $S'\bar{D}^\delta \partial x^\delta / \partial h$ in general instead for $\partial x^\delta / \partial h$ exactly, where S' is the effective sectional area. What is deduced from the continuity of $\partial x^\delta / \partial h$ in the text is, however, that $\partial x^\delta / \partial h \rightarrow 0$, for $h(<h_e) \rightarrow h_e$ and that $\partial x^A / \partial h < 0$ for $h(<0) \rightarrow 0$ from $\partial x^A / \partial h < 0$ for $h_e > h \geq 0$. As these conclusions invariably follow from the continuity of $S'\bar{D}^\delta \partial x^\delta / \partial h$ for the proved positive finite value of \bar{D}^A , the arguments in the text remain valid, if based formally upon the latter general condition.

$\partial x^\delta/\partial h$ and the smallest negative $C'D^\delta/x^\delta \cdot \partial x^\delta/\partial h$, since $C'D^\delta/x^\delta$ are all positive. Let g or s be δ relevant to the respective $C'D^\delta/x^\delta \cdot \partial x^\delta/\partial h$. It follows that

$$\partial x^g/\partial h > 0, \quad \partial x^s/\partial h < 0, \quad (24)$$

and hence according to (22. y) and (24) that the excess of $C'D^g/x^g \cdot \partial x^g/\partial h$ over $C'D^s/x^s \cdot \partial x^s/\partial h$ increases with increasing h , so that the existence of g and s , and hence (24) continues to hold. The part of g or s may happen to be transferred from one to the other δ along with the increase of h but (24) remains invariably valid.

The result is that sooner or later x^g exceeds unity or x^s becomes negative, which is of course absurd. Only physically significant solution of (22. y) is in consequence that of (21).

Next, we follow x^δ in the region, $h < h_e$.

It follows from (12) and (23), that

$$x^A = y^A + CS/n \cdot \bar{D}^A \partial x^A/\partial h, \quad (25. y)$$

where

$$\bar{D}^A = D^A(1-x^A) + \frac{D^N \partial x^N/\partial h + D^H \partial x^H/\partial h}{\partial x^N/\partial h + \partial x^H/\partial h} x^A. \quad (25. D)$$

On the basis of the continuity of $\partial x^\delta/\partial h$ and (25), it is shown as below, that x^A varies with h as given qualitatively in Fig. 4 in the region, $h < h_e$.

We first consider the region inside the catalyst's bed where $0 \leq h < h_e$.

On the ground of the foregoing conclusion (21) and the continuity of $\partial x^\delta/\partial h$, we have

$$(\partial x^\delta/\partial h)_{h \rightarrow h_e (h < h_e)} = 0. \quad (26)$$

\bar{D}^A is, on the other hand, positive there, since along with the zeroth order approximation of identifying x^δ respectively with y^δ in evaluating correction terms $[x]$ and $[t]$, $\partial x^N/\partial h$ and $\partial x^H/\partial h$ in (25. D) may be taken to be of equal sign similarly as $\partial y^N/\partial h$ and $\partial y^H/\partial h$ are according to (17) and (18). Let now $x^A > y^A$. The $\partial x^A/\partial h$ is then positive by (25. y) or x^A increases with h . But since y^A monotonously decreases with increasing h according to § 8, $x^A - y^A$ and hence $\partial x^A/\partial h$ remains positive with increasing h according to (25. y). The x^A must now continue to increase, while y^A decreases, thus never meeting the boundary condition (26). It is shown similarly, that the premise, $x^A = y^A$, leads also to the contradiction to the latter condition. It follows that $x^A < y^A$ and hence $\partial x^A/\partial h < 0$ by (25. y) over the region.

If on the other hand $\partial x^A/\partial h$ is sufficiently smaller than $\partial y^A/\partial h$ so that $\partial^2 x^A/\partial h^2 \leq 0$, while $\partial^2 y^A/\partial h^2 > 0$ as in Fig. 4, $\partial x^A/\partial h - \partial y^A/\partial h$ and in consequence $\partial^2 x^A/\partial h^2$ according to (25. y) monotonously decrease with increasing h in contradiction again to the boundary condition. The $(\partial x^A/\partial h)_{h=0}$ must hence be fitted in with by a definite negative value.

We consider next the region $h < 0$.

It follows from (20) in general that either $\partial x^\delta/\partial h$ are simultaneously zero or one of them at least is positive. Eq. (10) states now that ω must be positive, since, if otherwise,

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either all n^s must vanish, or one of them at least must be negative, in contradiction in either way to the present experimental condition. It follows further from (10) that $\partial x^N/\partial h > 0$, for $n^N=0$ over the region, that $\partial x^H/\partial h > 0$, since $\omega x^H > n^H$, i.e. hydrogen formed in the catalyst's bed in excess over the external supply of the rate $n^H=N_H$ must be driven forward implied in the mass flow of the rate ωx^H and in consequence that \bar{D}^A is positive according to (25. D). As $n^A=N_A$, besides $n^N=0$ and $n^H=N_H$ in this region, we have according to (5. y) and (11. n),

$$y_{h \leq 0}^A = N_A/(N_A+N_H), \quad n = N_A+N_H,$$

respectively constant. Eq. (25. y) is now integrated as

$$y_{h \leq 0}^A - x^A = (y_{h \leq 0}^A - x_i^A) \exp \left(- \frac{n}{CS} \int_h^0 \frac{dh}{\bar{D}^A} \right),$$

where x_i^A is x^A at $h=0$, which is smaller than $y_{h \leq 0}^A$ according to the foregoing conclusion, $\partial x^A/\partial h < 0$, for the region, $0 \leq h < h_e$, the continuity of $\partial x^s/\partial h$ and (25. y). The above equation states that $x^A (< y_{h \leq 0}^A)$ approaches the constant $y_{h \leq 0}^A$ steadily with decreasing h , because of the positive value of \bar{D}^A , as illustrated in Fig. 4.

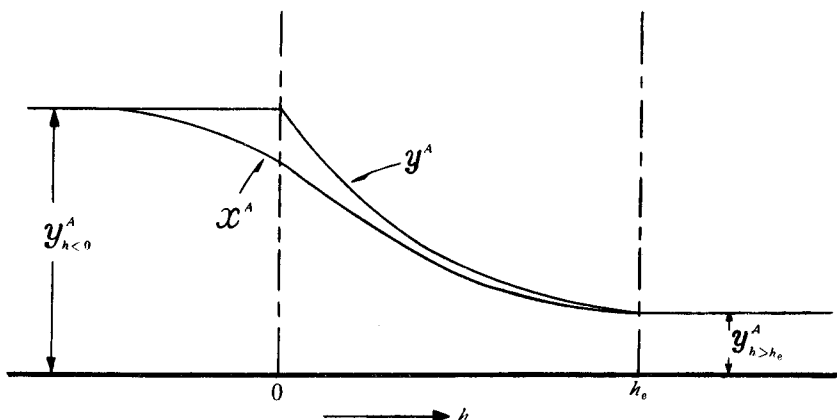


Fig. 4 Variation of ammonia mol fraction x^A and fraction y^A of its flow rate with depth h in the catalyst's bed.

The x^A deviates thus from y^A in general, the deviation varying with h and n as seen from (25). The function $U(t_m, x^A)$ must hence vary with the flow rate at given t_m and y^A , along with the variation of x^A .

§ 10. Evaluation of $[x]$

The correction $[x]$ of (9. x), i.e.

$$[x] = \int_{y_i^A}^{y_e^A} \frac{dy^A}{U^2(1+y^A)^2} \left(\frac{\partial U}{\partial x^A} \right)_{t_m} \left(\frac{\partial x^A}{\partial (1/N)} \right)_{y^A}$$

is now evaluated in zeroth order approximation of identifying y^A with x^A .

The U in the integral is first determined as U_e by (8) from a series of measurements of y_e^A at different N and nearly the same averages of t_1, t_2, t_3 and t_4 , regarding them as if conducted exactly at the same temperature, kept homogeneous throughout the catalyst's bed. U_e thus determined is now adjusted precisely as the function of $t_{m,e}$ and y_e^A in a manner described in §12 and identified with U as the function of t_m and y^A , which are respectively numerically equal to $t_{m,e}$ and y_e^A .

The factor $(\partial U / \partial x^A)_{t_m}$ in the integral is determined from the result of the above calculation, as

$$\left(\frac{\partial U}{\partial x^A} \right)_{t_m} = \left(\frac{\partial U}{\partial y^A} \right)_{t_m} . \quad (27)$$

The last factor $\{\partial x^A / \partial (1/N)\}_{y^A}$ in the integral is given as

$$\left\{ \frac{\partial x^A}{\partial (1/N)} \right\}_{y^A} = - \frac{2C\bar{D}^A S^2 U (1+y^A)^3}{N} , \quad (28. x)$$

where

$$\bar{D}^A = D^A(1-y^A) + \frac{5D^N + 7D^H}{12} y^A , \quad (28. D)$$

for the present experimental condition that N_H/N_A is kept constant at 4 throughout as shown below.

Identifying x^A with y^A , \bar{D}^A of (28. D) is expressed as

$$\bar{D}^A = D^A(1-y^A) + \frac{D^N + rD^H}{1+r} y^A , \quad (29. D)$$

where

$$r = \frac{\partial y^H}{\partial h} / \frac{\partial y^N}{\partial h} . \quad (29. r)$$

We have on the other hand from (11. n), (12), (4. H) and (5. A)

$$y^N + y^H + y^A = 1, \quad y^H = 3y^N + N_H/n, \quad n(1+y^A) = N, \quad (30. a), (30. b), (30. c)$$

or eliminating n and y^A from (30)

$$(1 + N_H/N)y^H = (3 - N_H/N)y^N + 2N_H/N.$$

The N_H/N in the above equation is, according to (5. N) and the experimental condition, $N_H/N_A = 4$, kept constant at 2/3 throughout the present experiment, so that

$$y^H = \frac{7y^N + 4}{5} . \quad (31)$$

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We have now from (31) and (29), $r=7/5$ or (28. D), which states that \bar{D}^A is the sole function of y^A independent of N at constant temperature, in so far as D^δ 's are functions of x^δ 's respectively identified with y^δ 's.

The factor $\{\partial x^A/\partial(1/N)\}_{y^A}$ in question is now according to (25. y)

$$\left\{ \frac{\partial x^A}{\partial(1/N)} \right\}_{y^A} = CS\bar{D}^A \frac{\partial x^A}{\partial h} \left\{ \frac{\partial(1/n)}{\partial(1/N)} \right\}_{y^A} + \frac{CS\bar{D}^A}{n} \left\{ \frac{\partial(\partial x^A/\partial h)}{\partial(1/N)} \right\}_{y^A} \quad (32)$$

The differential coefficient $\{\partial(1/n)/\partial(1/N)\}_{y^A}$ equals $1+y^A$ by (30. c), i. e.

$$\left\{ \frac{\partial(1/n)}{\partial(1/N)} \right\}_{y^A} = 1+y^A, \quad (33)$$

whereas $\partial x^A/\partial h$ is given by (6. y) identifying x^A with y^A as

$$\partial x^A/\partial h \doteq \partial y^A/\partial h = -SU/N \cdot (1+y^A)^2, \quad (34)$$

from which we have

$$\left\{ \frac{\partial(\partial x^A/\partial h)}{\partial(1/N)} \right\}_{y^A} = -SU(1+y^A)^2, \quad (35)$$

regarding U as the function of y^A for the present approximation. We have now (28. x) from (32), (33), (34) and (35) referring to (30. c).

The $[x]$ is now given from (9. x), (27) and (28. x) as

$$[x] = -\frac{2CS^2}{N} \int_{y_t^A}^{y_e^A} \frac{\bar{D}^A(1+y^A)}{U} \left(\frac{\partial U}{\partial y^A} \right)_{t_m} dy^A. \quad (36)$$

The \bar{D}^A is calculated by (28. D) and (15), assuming λ^δ in the thermal part as given by the usual expression,

$$\lambda_i^{\delta k} = \left[\pi C \sum_i y^{\delta i} \sigma_{ki}^2 (1 + m^{\delta k}/m^{\delta i})^{1/2} \right]^{-1} {}^{**}), \quad (37)$$

where δ_k is k -th δ , $m^{\delta k}$ or $m^{\delta i}$ the molecular weight and σ_{ki} the mean of the collision diameters σ_k and σ_i respectively of δ_k and δ_i , i. e. the appropriate pair of $\sigma_A = 4.43 \times 10^{-8}$ cm, $\sigma_N = 3.75 \times 10^{-8}$ cm and $\sigma_R = 2.74 \times 10^{-8}$ cm $^{**})$, concentration of δ being identified with Cy^δ .

§ 11. Determination of t_m

The t_m in (9) is determined as follows. As remarked in § 4, t_4 is pretty higher than t_1 , t_2 and t_3 , which are relatively near each other. On this ground the temperature distribution over every horizontal section through the catalyst's bed is approximated by that through

$^{*)}$ Cf. e.g. S. H. KENNARD, *Kinetic Theory of Gases*, McGraw-Hill, New York, 1939, p. 112.

$^{**})$ *ibid.* p. 149.

the catalyst's bed of infinite height, whose temperature varies radially but not vertically and is the same to that of the section in question on the axis as well as on the wall respectively, in accordance with the equation

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dt}{dr} \right) = Q/\kappa, \quad (38)$$

where t or r is the temperature or the radius from the axis to the point of interest, κ the effective specific thermal conductivity and Q the heat evolved per unit volume of the catalyst's bed per unit time. Integrating (38) assuming Q/κ constant^{*)}, we have

$$t = t_0 + (t_R - t_0) r^2 / R^2, \quad (39)$$

where t_0 or t_R is t at $r=0$ or $r=R$, i.e. that on the axis or the wall.

Assuming now local value U_t of U a linear function of temperature over the respective horizontal section, as

$$U_t = U_0 + \alpha (t - t_0), \quad (40)$$

we have by averaging U_t over the section according to (39) and (40)

$$U = \frac{1}{\pi R^2} \int_0^R U_t 2\pi r dr = U_0 + \frac{\alpha}{2} (t_R - t_0) = U_0 + \alpha \left(\frac{t_R + t_0}{2} - t_0 \right). \quad (41. U)$$

We see from (40) and (41. U) that averaged U over the section just corresponds to U_t at $\frac{t_R + t_0}{2}$ or we have, according to the definition of t_m in § 6,

$$t_m = \frac{t_R + t_0}{2}. \quad (41. t)$$

Temperature inhomogeneity along the axis, i.e. the variation of t_0 along h was allowed for by the quadratic function

*) Assuming instead Q/κ a linear function of temperature, as $Q/\kappa = A + Bt$ with constants A and B , in accordance with the linear form (40) of U , we have by solving (38)

$$t - t_0 = (t_R - t_0) \frac{r^2}{R^2} \frac{1 + F(r)}{1 + F(R)},$$

in place of (39), where

$$F(r) = \sum_{j=1}^{\infty} \frac{1}{\left(\frac{j}{2}!\right)^2} \left(\frac{Br^2}{2^2} \right)^{\frac{j}{2}-1}, \quad (j: \text{even})$$

provides higher order correction, which is ignored in the present approximation.

$$t_0 = ah^2 + bh + c, \quad (42)$$

whereas that of t_R is neglected as

$$t_R = t_4, \quad (43. R)$$

on the ground that the temperature on the wall is rather controlled from outside than affected from inside by the endothermic reaction, in accordance with the observed differences between t_1 etc.. The coefficients a , b and c of (42) are given in terms of temperatures t_1 , t_2 and t_3 as

$$a = \frac{2}{h_e^2} (t_1 + t_3 - 2t_2), \quad b = \frac{1}{h_e} (4t_2 - t_3 - 3t_1), \quad c = t_1. \quad (43. a), (43. b), (43. c)$$

Eqs. (41. t), (42) and (43) determine t_m as a function of h on the base of the observed values of t_1 , t_2 , t_3 and t_4 .

§ 12. Evaluation of $[t]$

The U in the correction term $[t]$ of (9. t), i. e.

$$[t] \equiv \int_{y_e^A}^{y_e^A} \frac{dy^A}{U^2 (1+y^A)^2} \left(\frac{\partial U}{\partial t_m} \right)_{x^A} \left(\frac{\partial t_m}{\partial (1/N)} \right)_{y^A}$$

is evaluated from the set of series of y_e^A , N -observations as follows.

U is first determined crudely as described in § 10 from each series of direct y_e^A , N -observations as the function of $t_{m,e}$ and y_e^A . The temperature coefficient of U_e is now determined from the U_e -values obtained as above at each y_e^A and by means of this temperature coefficient the above U_e -values are corrected to $t_{m,c}$ taken more or less arbitrarily within the scatter of nearly equal $t_{m,e}$ of each group. We have now a number of series, each appropriate to a definite $t_{m,c}$, of U_e -values at different y_e^A . The temperature coefficient is now recalculated from the series and by means of which original U_e -values are again corrected to the respectively appropriate $t_{m,c}$. This procedure is repeated until corrected U_e -values vary no more.

The functional relation between U_e , $t_{m,e}$ and y_e^A thus obtained holds between corresponding quantities without suffix e , in so far as U is the function of t_m and x^A identified with y^A .

The second factor $(\partial U / \partial t_m)_{x^A}$ in the integral is identified with $(\partial U_e / \partial t_{m,e})_{y_e^A}$ obtained in the above calculation.

The third factor $(\partial t_m / \partial (1/N))_{y^A}$ is developed as

$$\left(\frac{\partial t_m}{\partial (1/N)} \right)_{y^A} = \left(\frac{\partial t_m}{\partial h} \right)_N \left(\frac{\partial h}{\partial (1/N)} \right)_{y^A} + \left(\frac{\partial t_m}{\partial (1/N)} \right)_h, \quad (44)$$

regarding t_m as a function of h and N . The differential coefficients $(\partial t_m / \partial h)_N$ and $(\partial t_m / \partial (1/N))_h$ in the above equation are given according to (41. t) and (42) as

$$\left(\frac{\partial t_m}{\partial h} \right)_N = ah + \frac{1}{2}b, \quad (45. a)$$

$$\left(\frac{\partial t_m}{\partial (1/N)} \right)_h = \frac{1}{2}a'h^2 + \frac{1}{2}b'h + \frac{1}{2}c' + \frac{1}{2}t'_R, \quad (45. b)$$

where a , b , c , t_R and their differential coefficients $a' = (\partial a / \partial (1/N))_h$ etc. are determined by (43) from the observations of t_1 , t_2 , t_3 and t_4 , and of their variations with N . We have on the other hand

$$\left(\frac{\partial h}{\partial (1/N)} \right)_{y^A} = -hN, \quad (46)$$

since the indefinite integral of (6. y), i.e.

$$-\int_{y_e^A}^{y^A} \frac{dy^A}{U(1+y^A)^2} = \frac{Sh}{N} \quad (47)$$

is constant at constant y^A and hence h/N is similarly in the zeroth order approximation.

The $[t]$ is now expressed according to (9. t), (44), (45) and (46) as

$$[t] = \int_{y_e^A}^{y^A} \frac{dy^A}{2U^2(1+y^A)^2} \left(\frac{\partial U}{\partial t_m} \right)_{y^A} \{a'h^2 + b'h + c' + t'_R - (2ah + b)hN\}. \quad (48)$$

It is required for the evaluation of $[t]$ to determine the relation between y^A and h , inasmuch as the last factor of the integrand of (48) is given as the function of h . The latter relation was determined by means of the indefinite integral (47) substituting U -values for a properly fixed t_m for the zeroth order approximation, so as just to fit in with the observed values of V , N , y_e^A and y_e^A in accordance with the definite integral (7).

§ 13. Final Correction and the Results

The corrected value $U_{e, \text{corr.}}$ of U_e is now given according to (9. U), from the value of $[x]$ and $[t]$ just worked out, as

$$U_{e, \text{corr.}} = - \frac{dy_e^A / d(1/N)}{(V - [x] - [t])(1 + y_e^A)^2}. \quad (49)$$

Those data were rejected, for which $[x]$ appreciably exceeds 10% V , regarding possible uncertainty of (37) underlying the correction. The y_e^A, N -plots appropriate to the rejected data of U are indicated in Fig. 2 with dotted lines through the scatter of the latter plots.

The procedure of calculation described in the forgoing sections is now repeated on the base of $U_{e, \text{corr.}}$ in place of U_e to work out $[x]$, $[t]$ and hence further $U_{e, \text{corr.}}$ by (49). This successive approximation was carried forward, until the value of $[x]$ and $[t]$ remained unvaried by any further step of approximation. The invariant values of $[x]$ and $[t]$ were attained practically by the second step in most of cases.

Table 2 shows the final values of $[x]$ and $[t]$ in cc, $U_{e, \text{corr.}}$ calculated by (49) with the latter values, and the appropriate $t_{m, e}$, each section of the Table giving data of nearly equal $t_{m, e}$. The final values of U at every $t_{m, e}$ and y_e^A are worked out as shown in Table 3 according to the procedure described in §12 from the final value of $U_{e, \text{corr.}}$ in Table 2; in Table 3, y_e^A is replaced by x^A at $h=h_c$, which equals y_e^A according to (25.y) and (26).

TABLE 2. Final values of $[x]$, $[t]$ and $U_{e, \text{corr.}}$

$V=54.5$ cc.

y_e^A	0.183	0.172	0.150	0.135	0.133	0.126
$t_{m, e}$ °C	471	469	474	479	477	481
$[x]$ cc	0.4	1.2	3.8	6.6	7.7	8.2
$[t]$ cc	9.3	9.2	1.6	2.4	3.6	— 1.8
$U_{e, \text{corr.}}$ $\frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$	31.6	20.9	13.1	10.7	10.9	8.65

y_e^A	0.190	0.176	0.168	0.159
$t_{m, e}$ °C	441	451	448	445
$[x]$ cc	0.3	2.2	4.6	10.5
$[t]$ cc	0.6	4.7	1.3	1.6
$U_{e, \text{corr.}}$ $\frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$	8.62	6.79	4.94	2.80

y_e^A	0.176	0.145	0.121	0.098
$t_{m,e}$ °C	480	490	491	493
[x] cc	0.5	2.2	5.4	10.1
[t] cc	15.8	1.7	2.2	2.7
$U_{e, \text{corr.}} \frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$	54.3	25.5	19.7	15.3

y_e^A	0.145	0.113	0.090	0.061	0.060	0.032
$t_{m,e}$ °C	506	507	516	515	515	516
[x] cc	0.6	1.6	3.1	5.7	5.7	10.7
[t] cc	9.1	9.5	5.4	2.6	2.2	4.0
$U_{e, \text{corr.}} \frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$	76.6	57.3	41.2	26.6	23.7	17.7

y_e^A	0.107	0.068	0.024
$t_{m,e}$ °C	528	526	530
[x] cc	0.8	2.5	6.7
[t] cc	7.6	6.7	2.7
$U_{e, \text{corr.}} \frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$	105.0	68.0	29.0

TABLE 3. Final value of $U \frac{\text{mol NH}_3}{\text{cc min}} \times 10^6$

x^A	0.183	0.172	0.150	0.135	0.133	0.126
$t_{m,c}$						
475 °C	38.5	31.0	14.2	7.59	9.08	3.52

x^A	0.190	0.176	0.168	0.159
$t_{m,c}$				
446 °C	11.4	5.14	4.61	2.82

x^A	0.176	0.145	0.121	0.098
$t_{m,c}$				
489 °C	76.3	22.9	16.3	10.8

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x^A	0.145	0.113	0.090	0.061	0.060	0.032
$t_{m,c}$						
513 °C	101.3	70.6	34.2	22.0	19.6	14.1

x^A	0.107	0.068	0.024
$t_{m,c}$			
528 °C	104.6	71.5	27.3

We see from Table 2 that $[x]$ is quite insignificant, as referred to in § 7, for larger y_e^A to which larger N corresponds as seen from Fig. 2.

Summary

1. The bed of properly reduced, doubly promoted ammonia synthetic catalyst was flown with 1:4 ammonia-hydrogen mixture at 1 atm total pressure and 450~540°C and the steady ammonia outflow rate was determined at different inflow rates and temperatures of the catalyst's bed.

2. The rate of ammonia decomposition U_e per unit volume of the catalyst's bed was shown to be given as

$$U_e = - \frac{dy_e^A/d(1/N)}{V(1+y_e^A)^2}, \quad N = 2N_A + N_H,$$

at the steady state in the absence of turbulence, diffusion and inhomogeneity of temperature and flow rates inside the catalyst's bed, where y_e^A is the observed fraction of the ammonia outflow rate over the total outflow rate, to which U_e given by the above equation is appropriate, V the volume of the catalyst's bed and N_A or N_H the inflow rate of ammonia or hydrogen.

3. The deviation from the above U_e -value due to the turbulence and diffusion on one hand and to the temperature inhomogeneity on the other hand was theoretically analyzed.

4. The U_e -value corrected for the deviations mentioned above was given as the function of temperature and mol fraction of ammonia.

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