<table>
<thead>
<tr>
<th>Title</th>
<th>THE MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST: Ⅰ: OBSERVATION OF THE DECOMPOSITION RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>HORIUTI, Juro; TOYOSHIMA, Isamu</td>
</tr>
<tr>
<td>Citation</td>
<td>JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 5(3), 120-144</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1957-12</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/24665">http://hdl.handle.net/2115/24665</a></td>
</tr>
<tr>
<td>Type</td>
<td>bulletin (article)</td>
</tr>
<tr>
<td>File Information</td>
<td>5(3)_P120-144.pdf</td>
</tr>
</tbody>
</table>

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
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

(Received December 29, 1957)

Introduction

Enomoto, Kohayashi and one of the present authors have found the stoichiometric number of the rate-determining step of the catalyzed ammonia synthetic reaction

\[ \text{N}_2 + 3\text{H}_2 = 2\text{NH}_3 \quad (1) \]

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

\[ \begin{align*}
\text{N}_2 & \rightarrow 2\text{N}(a) \\
\text{H}_2 & \rightarrow 2\text{H}(a) \\
\text{N}(a) + \text{H}(a) & \rightarrow \text{NH}(a) \\
\text{NH}(a) + \text{H}(a) & \rightarrow \text{NH}_2(a) \\
\text{NH}_2(a) + \text{H}(a) & \rightarrow \text{NH}_3 \\
\end{align*} \quad (2) \]

(a): adsorbed state

provided that the catalyzed synthesis follows the sequence (2) at all.

It is the purpose of the present work to identify the rate-determining step in extention 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

*) J. H. and I. T.; Research Institute for Catalysis, Hokkaido University.
**) 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).
The Mechanism of Catalyzed Decomposition of Ammonia

less in excess in the case of catalyzed decomposition. The iron-ammonia-hydrogen system has been exhaustively investigated by Emmett and collaborators and a number of other authors with consistent results, which assures, in particular, that catalyst iron used by Enomoto, Horiuti and Kobayashi 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, i.e. doubly promoted iron catalyst containing 1.82% Al₂O₃, 1.06% K₂O, 0.41% SiO₂, 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 F₁ keeps the catalyst’s bed at a desired temperature and preheats inflow gas. J₁, J₂, J₃ and J₄ 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

- Reaction chamber
- Flow meters
- Soda lime
- Silica gel (each in two columns)
- Thermojunctions
- Traps
- Electric furnaces (F₁ or F₂ for Ni or Cu gauze)
- Pressure regulator (gas overflow)
- Potassium hydroxide
- Phosphorous pentoxide
- Manometers
respectively of the catalyst bed, \( J_1 \) being automatically kept at the desired temperature by means of a potentiometric thermostimulator within \( \pm 2 \)°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 \( N' \) 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 \textit{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 560°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.

\[ \frac{N_B}{N_A} = 4.00 \pm 0.023 \]

<table>
<thead>
<tr>
<th>No. of Runs</th>
<th>Date</th>
<th>Temperature °C</th>
<th>Inflow rate of ( \frac{N_B}{N_A} ) mol/min ( \times 10^3 )</th>
<th>Ammonia outflow rate ( \frac{N_A'}{N_A} ) mol/min ( \times 10^3 )</th>
<th>Fraction of ammonia outflow rate ( \frac{y_A}{N_A} )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>July 6</td>
<td>472</td>
<td>471 472 484 475</td>
<td>0.902 3.625 0.446</td>
<td>0.090</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>472</td>
<td>472 474 484 476</td>
<td>1.786 7.186 1.135</td>
<td>0.118</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>472</td>
<td>470 474 485 475</td>
<td>4.464 17.86 3.535</td>
<td>0.150</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>472</td>
<td>471 471 484 475</td>
<td>2.781 10.98 1.963</td>
<td>0.126</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>467</td>
<td>468 478 488 475</td>
<td>8.929 35.71 7.842</td>
<td>0.172</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>472</td>
<td>470 472 484 476</td>
<td>1.107 4.451 0.581</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>21</td>
<td>472</td>
<td>469 486 484 474</td>
<td>2.746 10.93 1.925</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td></td>
<td>460</td>
<td>463 486 484 476</td>
<td>18.08 72.54 16.81</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Oct. 30</td>
<td>472</td>
<td>472 472 481 474</td>
<td>3.130 12.41 2.222</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>July 8</td>
<td>447</td>
<td>447 447 457 450</td>
<td>0.911 3.692 0.710</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>447</td>
<td>447 450 460 451</td>
<td>1.263 5.022 1.005</td>
<td>0.153</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>447</td>
<td>447 450 458 450</td>
<td>2.746 16.16 2.377</td>
<td>0.163</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>447</td>
<td>447 448 460 451</td>
<td>1.786 7.186 1.474</td>
<td>0.159</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>447</td>
<td>447 450 462 451</td>
<td>4.464 17.85 4.013</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>22</td>
<td>445</td>
<td>445 450 462 450</td>
<td>8.929 35.71 8.553</td>
<td>0.190</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>July 13</td>
<td>485</td>
<td>484 484 496 487</td>
<td>0.902 3.549 0.252</td>
<td>0.049</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>485</td>
<td>484 484 496 487</td>
<td>1.263 5.045 0.451</td>
<td>0.063</td>
<td></td>
</tr>
</tbody>
</table>

Probable error of \( y_A^1 \): 1.2%

Several Runs at \( N_B/N_A = 10 \) and 457°C or 474°C inserted between Runs 36 and 37

Probable error of \( y_A^2 \): 1.1%

Probable error of \( y_A^3 \): 1.8%

\[ y_A^1 = \frac{N_A'}{2N_A-N_A'+N_B} \]

Journal of the Research Institute for Catalysts
<table>
<thead>
<tr>
<th>No</th>
<th>Date</th>
<th>Runs</th>
<th>Average</th>
<th>Duration</th>
<th>Temperature</th>
<th>Rate</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>July 13</td>
<td>486</td>
<td>484</td>
<td>496</td>
<td>487</td>
<td>1.786</td>
<td>7.188</td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>485</td>
<td>484</td>
<td>485</td>
<td>488</td>
<td>4.464</td>
<td>1.785</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>485</td>
<td>482</td>
<td>484</td>
<td>486</td>
<td>2.746</td>
<td>10.98</td>
</tr>
<tr>
<td>17</td>
<td>&quot;</td>
<td>484</td>
<td>483</td>
<td>486</td>
<td>487</td>
<td>8.973</td>
<td>3.710</td>
</tr>
<tr>
<td>18</td>
<td>&quot;</td>
<td>480</td>
<td>479</td>
<td>489</td>
<td>501</td>
<td>18.08</td>
<td>72.54</td>
</tr>
<tr>
<td>19</td>
<td>July 15</td>
<td>509</td>
<td>505</td>
<td>509</td>
<td>521</td>
<td>0.911</td>
<td>3.661</td>
</tr>
<tr>
<td>20</td>
<td>&quot;</td>
<td>509</td>
<td>505</td>
<td>509</td>
<td>521</td>
<td>1.263</td>
<td>4.044</td>
</tr>
<tr>
<td>21</td>
<td>&quot;</td>
<td>510</td>
<td>506</td>
<td>509</td>
<td>521</td>
<td>1.786</td>
<td>7.198</td>
</tr>
<tr>
<td>22</td>
<td>&quot;</td>
<td>511</td>
<td>506</td>
<td>509</td>
<td>521</td>
<td>4.457</td>
<td>17.95</td>
</tr>
<tr>
<td>23</td>
<td>16</td>
<td>502</td>
<td>501</td>
<td>516</td>
<td>530</td>
<td>18.04</td>
<td>72.54</td>
</tr>
<tr>
<td>24</td>
<td>&quot;</td>
<td>509</td>
<td>504</td>
<td>511</td>
<td>521</td>
<td>8.973</td>
<td>35.71</td>
</tr>
<tr>
<td>25</td>
<td>&quot;</td>
<td>510</td>
<td>506</td>
<td>509</td>
<td>521</td>
<td>2.746</td>
<td>10.98</td>
</tr>
<tr>
<td>26</td>
<td>17</td>
<td>509</td>
<td>506</td>
<td>509</td>
<td>521</td>
<td>6.696</td>
<td>21.88</td>
</tr>
<tr>
<td>27</td>
<td>&quot;</td>
<td>509</td>
<td>504</td>
<td>509</td>
<td>521</td>
<td>1.339</td>
<td>5.857</td>
</tr>
<tr>
<td>28</td>
<td>28</td>
<td>509</td>
<td>506</td>
<td>509</td>
<td>521</td>
<td>4.454</td>
<td>17.95</td>
</tr>
<tr>
<td>29</td>
<td>July 18</td>
<td>530</td>
<td>526</td>
<td>530</td>
<td>542</td>
<td>2.679</td>
<td>19.98</td>
</tr>
<tr>
<td>30</td>
<td>&quot;</td>
<td>533</td>
<td>526</td>
<td>530</td>
<td>542</td>
<td>4.531</td>
<td>13.08</td>
</tr>
<tr>
<td>31</td>
<td>&quot;</td>
<td>531</td>
<td>524</td>
<td>530</td>
<td>546</td>
<td>3.929</td>
<td>35.71</td>
</tr>
<tr>
<td>32</td>
<td>&quot;</td>
<td>526</td>
<td>526</td>
<td>533</td>
<td>548</td>
<td>18.04</td>
<td>72.54</td>
</tr>
</tbody>
</table>

*) 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 $y_1^A$ of ammonia outflow rate over the total outflow rate in the second last column is given as

$$\frac{N_A}{N} = 2N_A + NH$$

$N_A$, $NH$: ammonia or hydrogen inflow rate. Temperature designated: mean of "Averages" of each group in Table 1.
The Mechanism of Catalyzed Decomposition of Ammonia

\[ y_A^d = \frac{N_A'}{2N_A - N_A' + N_H}, \quad (3) \]

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 \( y_A^d \) 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 \( x^d \) of ammonia.

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

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

(III) The \( x^d \) of any gas component \( \delta \) equals everywhere the fraction \( y^d \) 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 \( n^A \) is the flow rate of \( A \), 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
\[
N = 2N_A + N_H. \tag{5. N}
\]

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.

\[
-dn^A = USdh, \tag{6. n}
\]

\( h \) being the depth of a horizontal section measured from the top of the catalyst's bed downwards. We have hence according to (5.4)

\[
-N\frac{dy^A}{(1+y^A)^2} = SUdh, \tag{6. y}
\]
or by integration

\[
-N\int_{y^A_i}^{y^A_e} \frac{dy^A}{U(1+y^A)^2} = \frac{V}{N}, \tag{7}
\]

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

\[
U_e = \frac{dy^A_e d(1/N)}{V(1+y^A_e)^2}, \tag{8}
\]
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 \( y^A \) 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),

\[
-\frac{1}{U_e(1+y^A_e)^2} \frac{dy^A_e}{d(1/N)} + [x] + [t] = V, \tag{9. U}
\]

where

\[
[x] = \int_{y^A_i}^{y^A_e} \frac{dy^A}{U(1+y^A)^2} \left( \frac{\partial U}{\partial x^A} \right)_{t_m} \left( -\frac{\partial x^A}{\partial (1/N)} \right)_{x^A} \tag{9. x}
\]
The Mechanism of Catalyzed Decomposition of Ammonia

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

\[ (9, t) \]

\( U, y^A \) 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 \( x^5 \) and \( y^5 \)

We investigate the relation between \( x^5 \) and \( y^5 \) qualitatively before evaluating \([x]\).

The \( x^5 \) must of course equal \( y^5 \), if every layer of gas mixture is moving downwards without any mix-up or mass interchange between the layers. Any deviation of \( x^5 \) from \( y^5 \) 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, \(-D^5CS\Delta x^5/\delta h\), 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. \( D^5 \) is the proportionality constant depending on the extent of the mix-up, or the additional rate across unit area at unit descent, \(-C\Delta x^5/\delta h\), of \( \delta \) concentration, and is nothing but the diffusion constant, if the mix-up is effected solely by the thermal motion. The resultant flow rate \( n^5 \) is now given as

\[ n^5 = -CSD^5 \frac{\Delta x^5}{\delta h} + \omega x^5 , \]

from which we have for the rate \( \omega \) of mass flow

\[ \omega = n + CS \sum D^5 \frac{\Delta x^5}{\delta h} , \]

where

\[ n \equiv \sum n^5 \equiv n^A + n^N + n^R . \]
We have from the definition of \( y^g \), (10) and (11, \( \omega \))
\[
y^g \equiv n^b / n = x^b - CS / n \cdot (D^g \partial x^g / \partial h - x^b \Sigma D^q \partial x^q / \partial h).
\] (12)

It has been shown by KANEKO\textsuperscript{5} and POLISSAR\textsuperscript{5} independently, that \( D^g \) due to different kinds of random zig-zag motions, 1, 2, \ldots, \text{..}, \text{I}, of constituent particles is given as
\[
D^g = \frac{1}{6} \sum_{i}^{I} \nu_i^\beta (l_i^\beta)^g,
\] (13)

where \( l_i^\beta \) is the length of the segment of a single rectilinear motion of \( i \)-th kind and \( \nu_i^\beta \) 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
\[
D^g = \frac{1}{6} \sum_{t}^{t} \nu_t^\beta (l_t^\beta)^g + \frac{1}{6} \sum_{p}^{p} \nu_p^\beta (l_p^\beta)^g,
\] (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 KANEKO\textsuperscript{5}, with special reference to gaseous molecules, as
\[
\sum_{t} \nu_t^\beta (l_t^\beta)^g = 2 \bar{v}_t^\beta \lambda_t^\beta,
\]
where \( \bar{v}_t^\beta \) is the mean velocity of \( \beta \) and \( \lambda_t^\beta \) the mean free path in accordance with the gas kinetic theory. Assuming that the similar transformation is valid to the summation \( \sum_{p} \nu_p^\beta (l_p^\beta)^g \), we have from (14)
\[
D^g = \frac{1}{3} (\bar{v}_t^\beta \lambda_t^\beta + \bar{v}_p^\beta \lambda_p^\beta),
\] (15)

where \( \bar{v}_p^\beta \) or \( \lambda_p^\beta \) is the relevant mean velocity or mean free path respectively corresponding to \( \bar{v}_t^\beta \) or \( \lambda_t^\beta \).

The \( \lambda_t^\beta \), \( \lambda_p^\beta \) and \( \bar{v}_t^\beta \) are respectively determined at \( 5.92 \times 10^{-6}, 8.5 \times 10^{-6}, 16.0 \times 10^{-6} \) cm in the respective pure gases at 0°C and 1 atm pressure\textsuperscript{*}, from which we have \( \lambda_t^\beta \bar{v}_t^\beta = 1.5, \lambda_p^\beta \bar{v}_p^\beta = 1.9 \) and \( \lambda_p^\beta \bar{v}_p^\beta = 13 \) cm\( ^2 \) sec\( ^{-1} \) in the respective pure gases at 500°C and 1 atm, assuming \( \lambda_t^\beta \) inversely proportional to the concentration and \( \bar{v}_t^\beta \) given as \( \bar{v}_t^\beta = \sqrt{8kT/\pi m_t^\beta} \), where \( k \) is the BOLTZMANN's constant and \( m_t^\beta \) the mass of the molecule \( \beta \). The

\* Smithsonian Physical Tables, Washington, D. C. 1933.
The Mechanism of Catalyzed Decomposition of Ammonia

\( \lambda^2 \) is estimated on the other hand at 1 cm\(^2\) sec\(^{-1}\) at most, identifying \( \lambda^2 \) with the average diameter 0.5 cm of the catalyst's grains and \( \bar{v}_g \) with the linear velocity of the gas flow, i.e. 2 cm sec\(^{-1}\) at most.

The values \( \lambda^2 \), in gas mixture of the present experiment being respectively, around the above values of pure gas at 500°C as calculated in later sections, \( D^2 \) 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 \( D^2 \) 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 in the corrected result of \( U \).

\[ \frac{\partial}{\partial h} \]

\( \delta \) Variation of \( y^5 \) with \( h \)

We might now qualitatively follow the variation of \( y^5 \) with \( h \).

We have for \( y^4 \), in particular, from (5. A)

\[ y^4 = \frac{n^4}{(N-n^4)}, \quad (16. A) \]

and similarly for \( y^5 \) and \( y^6 \) from (12), (11. n) and (4)

\[ y^5 = \frac{n^5}{2n^5+N+N}, \quad y^6 = \frac{3n^6}{2n^5+N+N}, \quad (16. N), (16. H) \]

or by differentiation

\[ \frac{dy^4}{dh} = \frac{N}{(N-n^4)^2} \frac{dn^4}{dh}, \quad (17. A) \]

\[ \frac{dy^5}{dh} = \frac{N+n^5}{(2n^5+N+n)} \frac{dn^5}{dh}, \quad \frac{dy^6}{dh} = \frac{3(N+N)}{(2n^5+N+n)^2} \frac{dn^5}{dh}. \quad (17. N), (17. H) \]

As coefficients of \( \frac{dn^5}{dh} \) in (17) are all positive and finite*, \( \frac{dy^5}{dh} \) and \( \frac{dn^5}{dh} \) have the same sign and the discontinuity, if any, at the same \( h \). The variation of \( y^5 \) may hence be reproduced qualitatively in this regard by that of \( n^5 \).

Fig. 3 shows the variation of \( n^5 \) deduced as follows. According to (6. n), \( n^4 \) varies continuously with \( h \) with finite differential coefficient

\[ \frac{\partial}{\partial h} \]

\( *) N-n^4 \) in (17. A) is positive and finite according to (4. A) and (5. N)
Fig. 3 Variation of flow rate $n_3$ of component $3$ with depth $h$ in catalyst's bed.

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

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

The flow rate $n_3$ 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 (6.11), 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 $\partial n_3/\partial h$ is discontinuous at the inlet or the exit of the catalyst's bed, i.e. at $h=0$ or $h$, respectively, as seen from (6.11) and (18), because of positive finite or zero $U$ respectively inside or outside the catalyst's bed. The $n_3$ 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 $x^A$ with $h$ qualitatively with
The Mechanism of Catalyzed Decomposition of Ammonia

reference to that of \( y^3 \) deduced in the forgoing section.

In the extreme case, when \( CSD^3 \partial x^3/\partial h \) in (10) is negligible, we have by (11.n) and (12)

\[
x^3 = y^3 ,
\]

noting

\[
\sum x^3 = 1 ,
\]

by definition.

For the general case it is to be noted, that \( \partial x^3/\partial h \) must be everywhere continuous at the steady state in distinction from \( \partial y^3/\partial h \), since otherwise \( \delta \) must accumulate at or dissipate from the point of the discontinuity of \( \partial x^3/\partial h \) 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 \( x^3 \) is constant and equals \( y^3 \) over the region, \( h > h_e \), i.e.

\[
x^3 = y^3 = \text{const.}, \quad h > h_e .
\]

We have from (10) and (12)

\[
\frac{y^A + C'D^A \partial x^A/\partial h}{x^A} = \frac{y^N + C'D^N \partial x^N/\partial h}{x^N} = \frac{y^H + C'D^H \partial x^H/\partial h}{x^H} ,
\]

where

\[
C' = CS/\pi .
\]

It follows, on the other hand, from the relation

\[
\partial x^A/\partial h + \partial x^N/\partial h + \partial x^H/\partial h = 0 ,
\]

derived from (20), that there exists positive as well as negative \( \partial x^3/\partial h \), unless all \( \partial x^3/\partial h \) simultaneously vanish. In the latter case, we have simply (21) from (20) and (22.y), noting constant \( y^3 \) in this region. In the former case, we have the greatest positive \( C'D^3/x^3 \times

*) This statement is exact, if the spaces above and beneath the catalyst's bed in \( \mathbf{R} \) were packed with such catalytically inactive grains, as providing the same turbulence and hence the same \( D^3 \) 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 \( S'D^3 \partial x^3/\partial h \) in general instead for \( \partial x^3/\partial h \) exactly, where \( S' \) is the effective sectional area. What is deduced from the continuity of \( \partial x^3/\partial h \) in the text is, however, that \( \partial x^3/\partial h \rightarrow 0 \), for \( h < h_e \rightarrow h_e \), and that \( \partial x^3/\partial h < 0 \) for \( h < 0 \rightarrow 0 \) from \( \partial x^3/\partial h < 0 \) for \( h > h_e \rightarrow h_e \). As these conclusions invariably follow from the continuity of \( S'D^3 \partial x^3/\partial h \) for the proved positive finite value of \( D^3 \), the arguments in the text remain valid, if based formally upon the latter general condition.

—133—
and hence according to (22, y) and (24) that the excess of $C'D^3/x^3 \cdot \partial x^3/\partial h$ over $C'D^4/x^4 \cdot \partial x^4/\partial h$ 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 $\delta$ along with the increase of $h$ but (24) remains invariably valid.

The result is that sooner or later $x^\delta$ exceeds unity or $x^4$ becomes negative, which is of course absurd. Only physically significant solution of (22, y) is in consequence that of (21).

Next, we follow $x^\delta$ in the region, $h<h_c$.

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

$$x^4 = y^4 + CS/n \cdot D^A \partial x^3/\partial h,$$

where

$$D^A = D^4(1-x^4) + \frac{D^3 \partial x^3/\partial h + D^2 \partial x^2/\partial h}{\partial x^3/\partial h + \partial x^2/\partial h} x^4.$$  (25, D)

On the basis of the continuity of $\partial x^3/\partial h$ and (25), it is shown as below, that $x^4$ varies with $h$ as given qualitatively in Fig. 4 in the region, $h<h_c$.

We first consider the region inside the catalyst’s bed where $0<h<h_c$.

On the ground of the foregoing conclusion (21) and the continuity of $\partial x^3/\partial h$, we have

$$\partial x^3/\partial h)_{h_{h_c}} = 0.$$  (26)

$D^A$ is, on the other hand, positive there, since along with the zeroth order approximation of identifying $x^\delta$ respectively with $y^\delta$ in evaluating correction terms $[x]$ and $[t]$, $\partial x^y/\partial h$ and $\partial x^y/\partial h$ in (25, D) may be taken to be of equal sign similarly as $\partial y^y/\partial h$ and $\partial y^y/\partial h$ are according to (17) and (18). Let now $x^4>y^4$. The $\partial x^4/\partial h$ is then positive by (25, y) or $x^4$ increases with $h$. But since $y^\delta$ monotonously decreases with increasing $h$ according to § 8, $x^4-y^4$ and hence $\partial x^4/\partial h$ remains positive with increasing $h$ according to (25, y). The $x^4$ must now continue to increase, while $y^4$ decreases, thus never meeting the boundary condition (26). It is shown similarly, that the premise, $x^4=y^4$, leads also to the contradiction to the latter condition. It follows that $x^4<y^4$ and hence $\partial x^4/\partial h<0$ by (25, y) over the region.

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

We consider next the region $h<h_c$.

It follows from (20) in general that either $\partial x^3/\partial h$ are simultaneously zero or one of them at least is positive. Eq. (10) states now that $\omega$ must be positive, since, if otherwise,
either all \( n^3 \) 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 \( \omega x^H \) and in consequence that \( \bar{D}^A \) is positive
according to (25. D). As \( n^A=N_A \), besides \( n^X=0 \) and \( n^H=N_H \) in this region, we have ac-
cording to (5. y) and (11. n),
\[
y_{A\leq0}^A = N_A/(N_A+N_H), \quad n = N_A+N_H,
\]
respectively constant. Eq. (25. y) is now integrated as
\[
y_{A\leq0}^A - x^A = (y_{A\leq0}^A-x_i^A) \exp \left( - \frac{n}{CS} \int_h^{0} \frac{dh}{D^A} \right),
\]
where \( x_i^A \) is \( x^A \) at \( h=0 \), which is smaller than \( y_{A\leq0}^A \) according to the foregoing conclusion,
\( \partial x^A/\partial h < 0 \), for the region, \( 0\leq h < h_c \), the continuity of \( \partial x^A/\partial h \) and (25. y). The above equation
states that \( x^A(<y_{A\leq0}^A) \) approaches the constant \( y_{A\leq0}^A \) 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.](image)

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 \( x^A \).

\section{10. Evaluation of \([x]\)}

The correction \([x]\) of (9. x), i.e.
\[
[x] = \int y_i^A \frac{dy^A}{U^2(1+y^A)^2} \left( \frac{\partial U}{\partial x^A} \right)_t \left( \frac{\partial x^A}{\partial (1/N)} \right)_y.
\]
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 $\left(\frac{\partial U}{\partial x^A}\right)_{t_m}$ in the integral is determined from the result of the above calculation, as

$$\frac{\partial U}{\partial x^A} = \frac{\partial U}{\partial y^A}_t$$

(27)

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

$$\{\frac{\partial x^A}{\partial (1/N)}\} y^A = -\frac{2CD^A S U (1+y^A)^3}{N},$$

(28. x)

where

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

(28. D)

for the present experimental condition that $N_{II}/N_d$ is kept constant at 4 throughout as shown below.

Identifying $x^A$ with $y^A$, $D^d$ of (25. D) is expressed as

$$D^A = D^A (1-y^A) + \frac{D^N+TD^H}{1+\gamma} y^A,$$

(29. D)

where

$$\gamma = \frac{\partial y^H}{\partial h} \bigg/ \frac{\partial y^N}{\partial h}.$$  

(29. r)

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

$$y^N+y^H+y^A = 1, \quad y^H = 3y^N+N_{II}/n, \quad n (1+y^d) = N, \quad \text{(30. a), (30. b), (30. c)}$$

or eliminating $n$ and $y^d$ from (30)

$$(1+N_{II}/N) y^H = (3-N_{II}/N) y^N + 2N_{II}/N.$$

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

$$y^H = \frac{7y^N+4}{5}. \quad \text{(31)}$$
The Mechanism of Catalyzed Decomposition of Ammonia

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

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

\[
\left\{ \frac{\partial x^A}{\partial (1/N)} \right\}_{y^A} = \text{CS} D^A \left( \frac{\partial (1/n)}{n} \right)_{y^A} + \text{CS} D^A \left( \frac{\partial (\partial x^A/\partial h)}{\partial (1/N)} \right)_{y^A}
\]

(32)

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

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

(33)

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

\[
\partial x^A/\partial h = \partial y^A/\partial h = -SU/N(1+y^A)^2,
\]

(34)

from which we have

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

(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

\[
[x] = -\frac{2CS^2}{N} \int_{n}^{y^A} \frac{D^A(1+y^A)}{U} \frac{\partial U}{\partial y^A} \, dy^A.
\]

(36)

The \( D^A \) is calculated by (28. D) and (15), assuming \( \lambda^3 \) in the thermal part as given by the usual expression,

\[
\lambda^3 = \left[ \pi C \sum_{k} x^A \sigma_{kl} (1+m_{kl}/m_{kl}^{1/2}) \right]^{-1},
\]

(37)

where \( \delta_k \) is \( k \)-th \( \delta \), \( m_{kl} \) or \( m_{kl}^{3/2} \) the molecular weight and \( \sigma_{kl} \) the mean of the collision diameters \( \sigma_k \) and \( \sigma_l \), i.e. the appropriate pair of \( \sigma_N = 4.43 \times 10^{-4} \text{cm}, \sigma_Y = 3.75 \times 10^{-8} \text{cm} \) and \( \sigma_R = 2.74 \times 10^{-8} \text{cm} \), concentration of \( \delta \) being identified with \( Cy^A \).

§ 11. Determination of \( t_m \)

The \( t_m \) in (9) is determined as follows. As remarked in § 4, \( t_i \) 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

\[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dt}{dr} \right) = \frac{Q}{\kappa}, \]  

(38)

where \( t \) or \( r \) is the temperature or the radius from the axis to the point of interest, \( \kappa \) the effective specific thermal conductivity and \( Q \) the heat evolved per unit volume of the catalyst's bed per unit time.

Integrating (38) assuming \( Q/\kappa \) constant\(^*\), we have

\[ t = t_0 + \frac{(t_R - t_0)}{R^2} r^2, \]  

(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

\[ U_t = U_0 + a (t - t_0), \]  

(40)

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

\[ U = \frac{1}{\pi R^2} \int_0^R U_t 2\pi r dr = U_0 + \frac{a}{2} (t_R - t_0) = U_0 + a \left( \frac{t_R + t_0}{2} - t_0 \right). \]  

(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,

\[ t_m = \frac{t_R + t_0}{2}. \]  

(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 \( Q/\kappa \) 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)

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

in place of (39), where

\[ F(r) = \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \frac{r}{2} \right)^j - \frac{1}{2^{j+1}}, \]  

\( (j: \) even \)

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

— 138 —
The Mechanism of Catalyzed Decomposition of Ammonia

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

whereas that of \( t_R \) is neglected as

\[ t_R = t_d, \quad (43, R) \]

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 \( t_i \) etc. The coefficients \( a, b \) and \( c \) of (42) are given in terms of temperatures \( t_i, t_e \) and \( t_s \) as

\[
\begin{align*}
    a &= \frac{2}{h_e^2}(t_1 + t_0 - 2t_s), \\
    b &= \frac{1}{h_e} (4t_s - t_0 - 3t_e), \\
    c &= t_1.
\end{align*}
\]

(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 \( t_i, t_e, t_s \) and \( t_t \).

§ 12. Evaluation of \([t]\)

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

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

is evaluated from the set of series of \( y^A_i, N \)-observations as follows.

\( U \) is first determined crudely as described in § 10 from each series of direct \( y^A_i, N \)-observations as the function of \( t_{m,e} \) and \( y^A_i \). The temperature coefficient of \( U_e \) is now determined from the \( U_e \)-values obtained as above at each \( y^A_i \) and by means of this temperature coefficient the above \( U_e \)-values are corrected to \( t_{m,e} \) 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 \( t_{m,e} \), of \( U_e \)-values at different \( y^A_i \). 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 \( t_{m,e} \). This procedure is repeated until corrected \( U_e \)-values vary no more.

The functional relation between \( U_e, t_{m,e} \) and \( y^A_i \) 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 \((\partial U/\partial t_m)_{y^A}\) in the integral is identified with \((\partial U/\partial t_m)_{y^A}\) obtained in the above calculation.

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

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

- 139 -
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

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

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

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

\[
\left( \frac{\partial h}{\partial (1/N)} \right)_{y_A} = -hN, \tag{46}
\]

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

\[
-h \int_{y_A}^{y_A'} \frac{dy^4}{2U(1+y^4)^2} = \frac{Sh}{N}, \tag{47}
\]

is constant at constant \( y^4 \) and hence \( h/N \) is similarly in the zeroth order approximation.

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

\[
[\ell] = \int_{y_A}^{y_A'} \frac{dy^4}{2U(1+y^4)^2} \left( \frac{\partial U}{\partial t_m} \right)_{y_A} \left\{ a'h^2 + b'h + c' + t'_R - (2ah + b)hN \right\}. \tag{48}
\]

It is required for the evaluation of \( [\ell] \) to determine the relation between \( y^4 \) 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 \( V, N, y_A \) and \( y_A' \) 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 \( [\ell] \) just worked out, as

\[
U_{e, \text{corr.}} = -\frac{dy^4/d(1/N)}{(V-[x]-[\ell])(1+y^4)^2}. \tag{49}
\]
Those data were rejected, for which $[x]$ appreciably exceeds 10% $V$, regarding possible uncertainty of (37) underlying the correction. The $y_i^eN$-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 foregoing sections is now repeated on the base of $U_{e, corr.}$ in place of $U_e$ to work out $[x]$, $[t]$ and hence further $U_{e, corr.}$ 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, $U_{e,corr.}$ calculated by (49) with the latter values, and the appropriate $t_m,c$, each section of the Table giving data of nearly equal $t_m,c$. The final values of $U$ at every $t_m,c$ and $y_i^e$ are worked out as shown in Table 3 according to the procedure described in §12 from the final value of $U_{e, corr.}$ in Table 2; in Table 3, $y_i^e$ is replaced by $x^e$ at $h = h_e$, which equals $y_i^e$ according to (25,$y$) and (26).

<table>
<thead>
<tr>
<th>$y_i^e$</th>
<th>0.183</th>
<th>0.172</th>
<th>0.159</th>
<th>0.185</th>
<th>0.183</th>
<th>0.126</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_m,c$ °C</td>
<td>471</td>
<td>469</td>
<td>474</td>
<td>479</td>
<td>477</td>
<td>481</td>
</tr>
<tr>
<td>$[x]$ cc</td>
<td>0.4</td>
<td>1.2</td>
<td>3.8</td>
<td>6.6</td>
<td>7.7</td>
<td>8.2</td>
</tr>
<tr>
<td>$[t]$ cc</td>
<td>9.3</td>
<td>9.2</td>
<td>1.6</td>
<td>2.4</td>
<td>3.6</td>
<td>-1.8</td>
</tr>
<tr>
<td>$U_{e, corr.}$ mol NH$_3$ × 10$^6$</td>
<td>3.16</td>
<td>20.9</td>
<td>13.1</td>
<td>10.7</td>
<td>10.9</td>
<td>8.65</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$y_i^e$</th>
<th>0.190</th>
<th>0.176</th>
<th>0.168</th>
<th>0.159</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_m,c$ °C</td>
<td>441</td>
<td>451</td>
<td>448</td>
<td>445</td>
</tr>
<tr>
<td>$[x]$ cc</td>
<td>0.3</td>
<td>2.2</td>
<td>4.6</td>
<td>10.5</td>
</tr>
<tr>
<td>$[t]$ cc</td>
<td>0.6</td>
<td>4.7</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>$U_{e, corr.}$ mol NH$_3$ × 10$^6$</td>
<td>8.82</td>
<td>6.79</td>
<td>4.94</td>
<td>2.80</td>
</tr>
<tr>
<td>( y_e^A )</td>
<td>0.176</td>
<td>0.145</td>
<td>0.121</td>
<td>0.098</td>
</tr>
<tr>
<td>( t_{m,c} ) °C</td>
<td>480</td>
<td>490</td>
<td>491</td>
<td>493</td>
</tr>
<tr>
<td>([x]) cc</td>
<td>0.5</td>
<td>2.2</td>
<td>5.4</td>
<td>10.1</td>
</tr>
<tr>
<td>([t]) cc</td>
<td>15.8</td>
<td>1.7</td>
<td>2.2</td>
<td>2.7</td>
</tr>
<tr>
<td>( U_{e,\text{corr.}} \text{ mol NH}_3 \times 10^6 )</td>
<td>54.3</td>
<td>25.5</td>
<td>19.7</td>
<td>15.3</td>
</tr>
</tbody>
</table>

| \( y_e^A \) | 0.145 | 0.113 | 0.090 | 0.061 | 0.060 | 0.082 |
| \( t_{m,c} \) °C | 506 | 507 | 516 | 515 | 515 | 516 |
| \([x]\) cc | 0.6 | 1.6 | 3.1 | 5.7 | 5.7 | 10.7 |
| \([t]\) cc | 2.1 | 2.5 | 5.4 | 2.6 | 2.2 | 4.0 |
| \( U_{e,\text{corr.}} \text{ mol NH}_3 \times 10^6 \) | 76.6 | 57.3 | 41.2 | 26.6 | 23.7 | 17.7 |

| \( y_e^A \) | 0.107 | 0.068 | 0.024 |
| \( t_{m,c} \) °C | 528 | 526 | 530 |
| \([x]\) cc | 0.3 | 2.5 | 6.7 |
| \([t]\) cc | 7.6 | 6.7 | 2.7 |
| \( U_{e,\text{corr.}} \text{ mol NH}_3 \times 10^6 \) | 105.0 | 68.0 | 29.0 |

**Table 3.** Final value of \( U_{e,\text{corr.}} \text{ mol NH}_3 \times 10^6 \)

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

| \( t_{m,c} \) °C | \( x^A \) | 0.190 | 0.176 | 0.163 | 0.159 |
| 446 °C | 11.4 | 5.14 | 4.61 | 2.82 |

| \( t_{m,c} \) °C | \( x^A \) | 0.176 | 0.145 | 0.121 | 0.098 |
| 489 °C | 76.3 | 22.9 | 16.3 | 10.8 |
We see from Table 2 that \([x]\) is quite insignificant, as referred to in § 7, for larger \(y_e^1\) 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

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

at the steady state in the absence of turbulence, diffusion and inhomogeneity of temperature and flow rates inside the catalyst's bed, where \(y_e^1\) 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.

The present authors wish to thank Dr. Tomiyuki Toya for his valuable advises and Mr. Takeshi Saito for his sincere and laborious assistance in calculation. Their thanks are also due to the Grant in Aid for Fundamental Scientific Research of the Ministry of Education.
References

2) S. ENOMOTO, J. HORIUTI and H. KOBAYASHI, this Journal 3, 185 (1955).
3) J. HORIUTI and M. IKUSHIMA, Proc. Imp. Acad. Tokio 15, 39 (1939); J. HORIUTI,
   this Journal 1, 8 (1948); J. HORIUTI and S. ENOMOTO, Proc. Japan Acad. 29, 160,
   164 (1953); J. HORIUTI and T. NAKAMURA, Z. physik. Chem. (Neue Folge) 11, 358
   (1957); J. HORIUTI, ibid. 12, 321 (1967); J. HORIUTI, this Journal 5, 1 (1957); T.
   NAKAMURA and H. YAMAZAKI, ibid. 5, 55 (1957).
4) P. H. EMMETT, S. B. HENDRICKS and S. BRUNAUER, J. Am. Chem Soc. 52, 1456
   (1930); S. BRUNAUER, M. E. JEFFERSON, P. H. EMMETT and S. B. HENDRICKS, J.
5) G. HÄGG, Z. physik. Chem. B 8, 455 (1930); E. LEHRER, Z. Elektrochem. 36, 383, 460
   (1930); O. EISENHUT and F. KAUPP, ibid. 36, 392 (1930); K. H. JACK, Proc. Roy.
   Soc. London A 195, 84 (1948); V. G. PARANITTE, M. COHEN, M. B. BEVER and C. F.
   FLORE, Trans. AIME 188, 391 (1950); A. BURDESSEX, Metallurgia ital 47, 357 (1955).
   Faraday Soc. 33, 1225 (1937).