MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST:Ⅲ: Hysteresis of the Decomposition Rate

Author(s)
TOYOSHIMA, Isamu; HORIUTI, Juro

Citation
JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(2), 146-160

Issue Date
1958-10

Doc URL
http://hdl.handle.net/2115/24678

Type
bulletin (article)

File Information
6(2)_P146-160.pdf
MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST.

III: Hysteresis of the Decomposition Rate

By

Isamu Toyoshima and Juro Horiuti *)

(Received September 15, 1958)

Introduction

It has been shown in the foregoing paper 1) that the catalyzed decomposition of ammonia in the presence of doubly promoted synthetic catalyst is governed by the dissociation of adsorbed imino group NH(a) into adsorbed nitrogen atom N(a) and hydrogen atom H(a), i.e.

\[ \text{NH(a)} \rightarrow \text{N(a)} + \text{H(a)} \]

This conclusion has been arrived at by analyzing the following experimental result 2) according to the generalized theory of reaction rate 3) on the basis of the previous conclusion of Enomoto, Horiuti and Kobayashi 4) that the stoichiometric number of the rate-determining step of the catalyzed ammonia synthesis or decomposition

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

is 2, which confines the part of determining the rate to the first three steps of the sequence

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

(2)

where (a) signifies the adsorbed state. Ammonia-hydrogen mixture of 1:4 mol ratio was allowed to flow 5) at different definite rates through a bed of the catalyst under the atmospheric pressure at 450°~540°C to

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

observe the outflow rate of ammonia until a steady value was attained at each definite inflow rate, and the decomposition rate of ammonia per unit quantity of the catalyst was determined from the result correcting for the effect of the deviation from the piston flow and the temperature homogeneity in the catalyst's bed.

It is well-known on the other hand that iron forms various iron nitrides\(^6\)\(^-\)\(^12\) depending on the temperature and the composition of gas around it. Observations of the ammonia decomposition over the synthetic catalyst\(^13\)\(^14\) have hitherto been carried out at the \(\alpha\)-phase state of the catalyst inclusive of the foregoing works\(^15\) of the present authors. Kobayashi and Nishizima\(^15\) have observed the decomposition of ammonia in ammonia-hydrogen mixtures of various compositions over a few different samples of ammonia synthetic catalysts from 380\(^\circ\) to 535\(^\circ\)C and found that the decomposition rate was unstable and varied hysteretically with composition of gas at the transition from \(\alpha\)- to \(\gamma\)'- or from \(\gamma\)'- to \(\varepsilon\)-phase of nitrides.

It has now been found by experiments similar to the previous one\(^9\) that the steady outflow rate of ammonia, finally attained at definite inflow rate and composition of inflow gas, revealed a quite stable and reproducible hysteresis at 1 atm total pressure and 487\(^\circ\)C, as the inflow rate of hydrogen was increased stepwise from one to another constant value and then decreased similarly at a fixed inflow rate of ammonia, and this result has been accounted for as described below on the basis of the mechanism of decomposition concluded in the foregoing paper\(^10\) and the known phase equilibrium of iron-nitrogen system.

§ 1. Experimental

The present experiments have been carried out in continuation to the foregoing experiment\(^7\) using the same apparatus with the same catalyst's bed.

After the previous experiment\(^7\), an observation of the hysteresis similar to that described below was preliminarily conducted and then the catalyst bed was flown with pure ammonia at 70 cc min\(^-1\) flow rate at 475\(^\circ\)C for 48 hours. The reaction chamber filled with ammonia was now cooled down to room temperature and left standing for ten months. Pure hydrogen was now allowed to flow over the catalyst at 200 cc min\(^-1\) rate at 550\(^\circ\)C for 48 hours, then cooled down to 487\(^\circ\)C and the gas flow was switched to that of 1 : 4 ammonia-hydrogen mixture to conduct a run just in the same way as in the foregoing experiment\(^7\).

Having thus kept check with activity of the catalyst, the catalyst was now subjected to the preliminary treatment described in the
foregoing paper, i.e. flowing it with pure hydrogen at 550°C for 4 to 5 hours and then the present observation of the hysteresis was started by lowering the temperature of the catalyst to 487°C and by switching the gas flow to that of ammonia-hydrogen mixture of specified composition. Each run of a definite composition of inflow gas was continued for 4 to 100 hours until the outflow rate \( N'_A \) of ammonia remained perfectly constant, when the inflow gas was switched to other composition by increasing or decreasing inflow rate \( N_H \) of hydrogen fixing that \( N_A \) of ammonia at 70 cc min\(^{-1}\) throughout.

The percent \( R \) of ammonia decomposition, i.e. \( R = 100 \frac{(N_A - N'_A)}{N_A} \) at the latter steady state finally attained for each constant composition of the inflow gas is given in Table 1 and plotted against the ratio \( N_H/N_A \) as shown in Fig. 1. Numbers of runs annexed to points in the figure show the order of them having been carried out.

These points lie, as shown in Fig. 1, reproducibly on a single curve BAA' which descends monotonously with increase of \( N_H/N_A \), so far as the runs were started at \( N_H/N_A \) greater than 4 and then conducted at

![Graph](image-url)
**Mechanism of Catalyzed Decomposition of Ammonia III**

**Table 1. Hysteresis of ammonia decomposition**

<table>
<thead>
<tr>
<th>No. of runs</th>
<th>Date</th>
<th>Temperature (^{\circ}\text{C})</th>
<th>Inflow rate (N_A) of (\text{NH}_3): (3.125\times10^{-3}) mol min(^{-1})=70.0 cc NTP min(^{-1})</th>
<th>Inflow rate (N_H) of (\text{H}_2) (\times10^{3})</th>
<th>Outflow rate (N_A) of (\text{NH}_3) (\times10^{3})</th>
<th>Percent decomposition of (\text{NH}_3) (\frac{N_A-N_A'}{N_A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dec. 10</td>
<td>484 484 484 496 496 487</td>
<td>12.41</td>
<td>3.97</td>
<td>1.793</td>
<td>42.6</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>484 484 484 496 496 487</td>
<td>4.656</td>
<td>1.49</td>
<td>1.414</td>
<td>54.8</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>484 484 486 496 488</td>
<td>3.156</td>
<td>1.91</td>
<td>1.745</td>
<td>44.2</td>
</tr>
<tr>
<td>4</td>
<td>17</td>
<td>484 484 486 496 488</td>
<td>1.788</td>
<td>0.57</td>
<td>1.659</td>
<td>46.9</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>484 484 481 496 486</td>
<td>1.788</td>
<td>0.57</td>
<td>1.794</td>
<td>42.6</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>484 484 481 496 486</td>
<td>0</td>
<td>0</td>
<td>1.370</td>
<td>56.2</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
<td>484 484 481 496 486</td>
<td>0.981</td>
<td>0.31</td>
<td>1.553</td>
<td>50.0</td>
</tr>
<tr>
<td>8</td>
<td>19</td>
<td>484 484 486 496 488</td>
<td>6.125</td>
<td>1.96</td>
<td>2.544</td>
<td>25.0</td>
</tr>
<tr>
<td>9</td>
<td>19</td>
<td>484 484 486 496 488</td>
<td>4.656</td>
<td>1.49</td>
<td>2.257</td>
<td>27.8</td>
</tr>
<tr>
<td>10</td>
<td>21</td>
<td>484 484 484 496 487</td>
<td>12.41</td>
<td>1.01</td>
<td>2.047</td>
<td>34.5</td>
</tr>
<tr>
<td>11</td>
<td>22</td>
<td>484 484 484 496 487</td>
<td>3.156</td>
<td>1.01</td>
<td>2.947</td>
<td>34.5</td>
</tr>
<tr>
<td>12</td>
<td>22</td>
<td>484 484 484 496 487</td>
<td>2.149</td>
<td>2.86</td>
<td>2.149</td>
<td>31.2</td>
</tr>
<tr>
<td>13</td>
<td>24</td>
<td>484 484 484 496 487</td>
<td>12.41</td>
<td>3.97</td>
<td>1.817</td>
<td>41.9</td>
</tr>
<tr>
<td>14</td>
<td>27</td>
<td>484 484 484 496 487</td>
<td>11.97</td>
<td>3.83</td>
<td>1.676</td>
<td>46.6</td>
</tr>
<tr>
<td>15</td>
<td>28</td>
<td>484 484 481 496 498</td>
<td>26.75</td>
<td>9.92</td>
<td>2.500</td>
<td>30.0</td>
</tr>
<tr>
<td>16</td>
<td>28</td>
<td>484 484 484 496 487</td>
<td>15.23</td>
<td>4.89</td>
<td>1.363</td>
<td>40.4</td>
</tr>
<tr>
<td>17</td>
<td>29</td>
<td>484 484 484 496 487</td>
<td>12.41</td>
<td>3.97</td>
<td>1.680</td>
<td>46.3</td>
</tr>
<tr>
<td>18</td>
<td>29</td>
<td>484 484 484 496 487</td>
<td>8.993</td>
<td>2.86</td>
<td>1.580</td>
<td>45.4</td>
</tr>
<tr>
<td>19</td>
<td>30</td>
<td>484 484 484 496 487</td>
<td>11.97</td>
<td>3.83</td>
<td>1.661</td>
<td>46.0</td>
</tr>
<tr>
<td>20</td>
<td>March 16</td>
<td>484 484 481 496 487</td>
<td>12.13</td>
<td>3.88</td>
<td>1.766</td>
<td>43.5</td>
</tr>
<tr>
<td>21</td>
<td>17</td>
<td>484 484 484 496 487</td>
<td>7.590</td>
<td>2.40</td>
<td>1.605</td>
<td>48.6</td>
</tr>
<tr>
<td>22</td>
<td>20</td>
<td>484 484 481 496 487</td>
<td>3.056</td>
<td>0.98</td>
<td>1.828</td>
<td>41.5</td>
</tr>
<tr>
<td>23</td>
<td>26</td>
<td>484 484 481 496 487</td>
<td>1.228</td>
<td>0.39</td>
<td>1.702</td>
<td>45.6</td>
</tr>
<tr>
<td>24</td>
<td>26</td>
<td>484 484 481 496 487</td>
<td>1.228</td>
<td>0.39</td>
<td>1.717</td>
<td>45.1</td>
</tr>
<tr>
<td>25</td>
<td>27</td>
<td>484 484 481 496 487</td>
<td>0</td>
<td>0</td>
<td>1.387</td>
<td>55.6</td>
</tr>
<tr>
<td>26</td>
<td>27</td>
<td>484 484 484 496 487</td>
<td>3.056</td>
<td>0.98</td>
<td>2.037</td>
<td>34.8</td>
</tr>
<tr>
<td>27</td>
<td>27</td>
<td>484 484 484 496 487</td>
<td>12.14</td>
<td>3.88</td>
<td>1.725</td>
<td>44.8</td>
</tr>
<tr>
<td>28</td>
<td>June 16</td>
<td>486 484 484 496 487</td>
<td>7.946</td>
<td>2.54</td>
<td>1.573</td>
<td>49.7</td>
</tr>
<tr>
<td>29</td>
<td>21</td>
<td>486 484 481 496 487</td>
<td>7.725</td>
<td>2.47</td>
<td>1.585</td>
<td>48.3</td>
</tr>
<tr>
<td>30</td>
<td>21</td>
<td>486 484 481 496 487</td>
<td>7.725</td>
<td>2.47</td>
<td>1.585</td>
<td>48.3</td>
</tr>
<tr>
<td>31</td>
<td>40</td>
<td>489 484 481 496 497</td>
<td>3.125</td>
<td>1.00</td>
<td>1.765</td>
<td>43.5</td>
</tr>
<tr>
<td>32</td>
<td>41</td>
<td>484 484 484 496 487</td>
<td>0</td>
<td>0</td>
<td>1.316</td>
<td>57.9</td>
</tr>
<tr>
<td>33</td>
<td>13</td>
<td>484 484 484 496 487</td>
<td>0</td>
<td>0</td>
<td>1.313</td>
<td>57.9</td>
</tr>
<tr>
<td>34</td>
<td>13</td>
<td>484 484 484 496 487</td>
<td>3.059</td>
<td>0.98</td>
<td>2.090</td>
<td>35.4</td>
</tr>
<tr>
<td>35</td>
<td>29</td>
<td>484 484 484 496 487</td>
<td>0</td>
<td>0</td>
<td>1.305</td>
<td>58.2</td>
</tr>
<tr>
<td>36</td>
<td>57</td>
<td>484 484 484 496 487</td>
<td>3.059</td>
<td>0.98</td>
<td>2.016</td>
<td>35.5</td>
</tr>
<tr>
<td>37</td>
<td>58</td>
<td>484 484 484 496 487</td>
<td>0</td>
<td>0</td>
<td>1.339</td>
<td>57.2</td>
</tr>
<tr>
<td>38</td>
<td>2</td>
<td>484 484 484 496 487</td>
<td>3.059</td>
<td>0.98</td>
<td>2.050</td>
<td>34.4</td>
</tr>
</tbody>
</table>

*) The \(t_1\), \(t_2\), \(t_3\), and \(t_4\) are temperatures read by thermojunctions inserted at different positions in the catalyst's bed of 54.5 cc total volume packed in a vertical quartz cylinder, gas mixture being passed through it from the top to the bottom; \(t_1\), \(t_2\), and \(t_3\) are readings of thermojunctions on the axis of the bed, respectively at the top, middle and bottom, and \(t_4\) is that on the wall at the middle. Cf. Ref. 2.
$N_{H}/N_{A}$ kept above 1.5 throughout. As $N_{H}/N_{A}$ was decreased below 1.5 at the point 3, the percent of ammonia decomposition continued to decrease for a long time down to a constant value appreciably lower than $R$ of the foregoing runs at higher $N_{H}/N_{A}$; it took 67 hours for the point 3 to attain its final value $R$ plotted in Fig. 1 which was then kept constant for further 30 hours as far as observed. Decreasing $N_{H}/N_{A}$ further, $R$ rose now as shown in the Figure up to the point D, where $N_{H}/N_{A}=0$. Increasing $N_{H}/N_{A}$ now reversely, former points on the curve DC were reproduced as far as ca. $N_{H}/N_{A}=0.5$ at C, but beyond that $R$ traced another curve CE lying below CBA. Points were now reproducibly on the single curve DCE descending monotonously with increasing $N_{H}/N_{A}$ so long as $N_{H}/N_{A}$ did not exceed 2. As it did, the $R$ increased above the point E as with the point 12, and with increase of $N_{H}/N_{A}$, $R$ restored the former value on BAA' thus completing the hysteresis.

It was found in the observation of the point 12 that the outflow rate of ammonia initially exceeded its inflow rate. This excess outflow of ammonia decreased rapidly to vanish within first 20 minutes of the observation, its $R$ being attained after 16 hours and kept for further

### Table 2. Percent decomposition of ammonia at $N_{H}/N_{A} = 2.5$

<table>
<thead>
<tr>
<th>No. of runs</th>
<th>Date</th>
<th>Temperature**</th>
<th>Inflow rate of Ammonia $N_{A}$</th>
<th>Outflow rate of Hydrogen $N_{H}$</th>
<th>Percent decomposition of NH$<em>3$ $R = \frac{N</em>{A} - N_{A}'}{N_{A}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>June 16</td>
<td>486, 484, 484, 496, 488</td>
<td>3.125, 7.946, 1.573</td>
<td>49.7</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>16</td>
<td>486, 484, 484, 496, 488</td>
<td>6.652, 16.67, 4.999</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>486, 484, 484, 496, 488</td>
<td>0.893, 2.232, 0.186</td>
<td>79.1</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>19</td>
<td>486, 484, 484, 496, 488</td>
<td>1.116, 2.768, 0.296</td>
<td>73.4</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>20</td>
<td>486, 484, 484, 496, 488</td>
<td>1.464, 3.741, 0.506</td>
<td>65.4</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>20</td>
<td>486, 484, 484, 496, 488</td>
<td>1.786, 4.464, 0.692</td>
<td>61.2</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>21</td>
<td>486, 484, 484, 496, 488</td>
<td>2.232, 5.598, 1.054</td>
<td>52.8</td>
<td></td>
</tr>
<tr>
<td>35*</td>
<td>21</td>
<td>484, 484, 484, 496, 488</td>
<td>3.125, 7.725, 1.585</td>
<td>49.3</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>21</td>
<td>486, 484, 484, 496, 488</td>
<td>4.464, 11.12, 2.846</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>21</td>
<td>479, 481, 486, 499, 488</td>
<td>17.86, 44.64, 15.38</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>22</td>
<td>486, 484, 484, 496, 488</td>
<td>2.500, 6.161, 1.218</td>
<td>51.3</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>23</td>
<td>486, 484, 484, 496, 488</td>
<td>3.540, 8.928, 2.067</td>
<td>41.6</td>
<td></td>
</tr>
</tbody>
</table>

*) Duplicated in Table 1.
**) Cf. footnote * to Table 1.
**Mechanism of Catalyzed Decomposition of Ammonia III**

**TABLE 3. Percent decomposition of ammonia at** $N_H = 0$

<table>
<thead>
<tr>
<th>No. of runs</th>
<th>Date</th>
<th>Temperature °C</th>
<th>Inflow rate $N_A$ of NH$_3$ mol min$^{-1}$</th>
<th>Outflow rate $N'_A$ of NH$_3$ mol min$^{-1}$</th>
<th>Percent decomposition of NH$_3$ $R = 100 \frac{N'_A-N_A}{N_A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 *)</td>
<td>Dec. 19 1953</td>
<td>484 484 481 496 486</td>
<td>3.125</td>
<td>1.370</td>
<td>56.2</td>
</tr>
<tr>
<td>25 *)</td>
<td>March 27 1954</td>
<td>486 484 481 496 486</td>
<td>3.125</td>
<td>1.387</td>
<td>55.6</td>
</tr>
<tr>
<td>41 *)</td>
<td>July 7 1954</td>
<td>484 484 484 496 487</td>
<td>3.125</td>
<td>1.316</td>
<td>57.9</td>
</tr>
<tr>
<td>42</td>
<td>7</td>
<td>486 484 484 496 488</td>
<td>8.882</td>
<td>5.156</td>
<td>42.0</td>
</tr>
<tr>
<td>43</td>
<td>8</td>
<td>486 484 481 496 487</td>
<td>4.465</td>
<td>2.185</td>
<td>50.8</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>489 484 481 499 488</td>
<td>23.13</td>
<td>15.83</td>
<td>31.6</td>
</tr>
<tr>
<td>45</td>
<td>10</td>
<td>489 484 484 499 488</td>
<td>12.54</td>
<td>7.777</td>
<td>36.4</td>
</tr>
<tr>
<td>46</td>
<td>10</td>
<td>489 484 479 501 488</td>
<td>44.20</td>
<td>34.46</td>
<td>22.0</td>
</tr>
<tr>
<td>47</td>
<td>10</td>
<td>489 484 481 496 488</td>
<td>5.603</td>
<td>28.46</td>
<td>49.2</td>
</tr>
<tr>
<td>48</td>
<td>12</td>
<td>486 484 484 496 488</td>
<td>3.540</td>
<td>1.652</td>
<td>53.3</td>
</tr>
<tr>
<td>49</td>
<td>12</td>
<td>486 484 484 496 488</td>
<td>1.750</td>
<td>0.642</td>
<td>63.3</td>
</tr>
<tr>
<td>50 *)</td>
<td>13</td>
<td>484 484 484 496 487</td>
<td>3.125</td>
<td>1.313</td>
<td>58.0</td>
</tr>
<tr>
<td>55</td>
<td>15</td>
<td>484 484 484 496 486</td>
<td>4.465</td>
<td>2.115</td>
<td>52.6</td>
</tr>
<tr>
<td>56 *)</td>
<td>28</td>
<td>484 484 484 484 487</td>
<td>3.125</td>
<td>1.305</td>
<td>58.2</td>
</tr>
<tr>
<td>58 *)</td>
<td>Aug. 2</td>
<td>484 484 484 496 486</td>
<td>3.125</td>
<td>1.339</td>
<td>57.2</td>
</tr>
</tbody>
</table>

*) Duplicated in Table 1. **) Cf. footnote *) to Table 1.

**TABLE 4. Percent decomposition of ammonia at** $N_H/N_A = 1$

<table>
<thead>
<tr>
<th>No. of runs</th>
<th>Date</th>
<th>Temperature °C</th>
<th>Inflow rate of Ammonia $N_A$ mol min$^{-1}$</th>
<th>Outflow rate of Hydrogen $N'_H$ mol min$^{-1}$</th>
<th>Percent decomposition of NH$_3$ $R = 100 \frac{N'_A-N_A}{N_A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 *)</td>
<td>Dec. 22 1953</td>
<td>484 484 484 496 487</td>
<td>3.125</td>
<td>3.170</td>
<td>2.047</td>
</tr>
<tr>
<td>26</td>
<td>March 27 1954</td>
<td>486 484 484 496 487</td>
<td>3.125</td>
<td>3.056</td>
<td>2.037</td>
</tr>
<tr>
<td>51 *)</td>
<td>July 13</td>
<td>486 484 484 496 487</td>
<td>3.103</td>
<td>3.058</td>
<td>2.018</td>
</tr>
<tr>
<td>52</td>
<td>13</td>
<td>484 484 484 496 487</td>
<td>8.929</td>
<td>8.929</td>
<td>7.400</td>
</tr>
<tr>
<td>54</td>
<td>14</td>
<td>484 484 484 496 487</td>
<td>0.893</td>
<td>0.893</td>
<td>0.402</td>
</tr>
<tr>
<td>57 *)</td>
<td>30</td>
<td>484 484 484 496 486</td>
<td>3.125</td>
<td>3.059</td>
<td>2.016</td>
</tr>
</tbody>
</table>

*) Duplicated in Table 1. **) Cf. footnote *) to Table 1.
12 hours as far as observed. The similar excess has been observed at
the second cycle of tracing the hysteresis, when the value of \( N_H/N_A \)
was switched from 1 at the point 26 to 4 at the point 27.

After the above determination of the points 28, 41 and 51 re­
spectively at \( N_H/N_A \) of 2.5, 0 and 1, the inflow rate of gas mixture of
constant composition was varied in each case just as in the previous
work\(^5\), before passing to the observation of next point. The steady
values \( R \) thus determined are shown in Table 2, 3 and 4 side by side
with data given in Table 1 respectively at the same \( N_H/N_A \).

The reproducibility of the results is established by the Figure
and these Tables. The result of the preliminary run with 1:4 mixture
provides a further check of the reproducibility, as mentioned above,
as compared with the run 37 in Table 1 of the foregoing paper\(^6\).

§ 2 Theoretical

The hysteresis observed is now accounted for on the basis of the
previous conclusions\(^7\) and the knowledge of the phase equilibria of iron­
nitrogen system\(^6\) under the postulates (I) that the sequence (2) is fol­
lowed whether the catalyst's surface is at the state of \( \alpha \)-phase or any
nitride, (II) that the rate-determining step is

\[
\text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a)
\]

on \( \alpha \)-phase and

\[
2\text{N}(a) \rightarrow \text{N}_2
\]
on any nitride, (III) that the backward rate of (4) is negligibelie compared
with its forward rate, (IV) that the steady rate of decomposition is
smaller when governed by (4) than by (3), and (V) that \( \text{N}(a) \) is in
equilibrium with constituent nitrogen atom \( \text{N}(F) \) of \( \alpha \)-phase or nitrides.

The steady rate \( V_s \) is given according to (I) and (III) with special
reference to (3) and (4) as\(^*)\)

\[
V_s = k_i(a_{\text{NH}} - a_\text{N}a_\text{H}) = k_i a_i^2,
\]

where \( a_{\text{NH}}, a_\text{N} \) and \( a_\text{H} \) are absolute activities of \( \text{NH}(a), \text{N}(a) \) and \( \text{H}(a) \)

\(\text{*) It is admitted for the present qualitative discussion, that the activity coefficient } f^* \text{ of the critical complex is constant throughout, the general expression for the rate } v \text{ of a thermal step being } v = ka^i/f^* \text{([cf. Ref. 4]), where } k \text{ is the rate constant and } a^i \text{ the activity product of the relevant initial complex.} \)
respectively defined by the relevant chemical potential $\mu^{NH}$ etc. as

$$\mu^{NH} = RT \ln a_{NH} \text{ etc.,} \tag{6}$$

and $k_1$ and $k_2$ are rate constants of Steps (3) and (4), which are respectively common to the forward and backward rates of the appropriate step. Since at equilibrium the forward and backward rates are equal to each other on the one hand, and absolute activities of the initial and final complexes are the same by the definition of (6), e.g. $a_{NH}$ and $a_{NH}$ then equal to each other, on the other hand.

Three steps of the scheme (2) other than (3) and (4) are now practically in equilibrium respectively according to (1) and (II), so that

$$a_{NH} = a_{NH} a_H, \quad a_{NH} = a_{NH} a_H, \quad a_H = a_{H}, \tag{7.a}, (7.b), (7.c)$$

where $a_{NH}$ is the absolute activity of NH$_2$(a) and $a_{NH}$ and $a_H$ are those of ammonia and hydrogen in gas. It follows from (7)

$$a_{NH} = a_{NH} a_H, \quad a_H = a_{H}^{1/2}, \tag{8.a}, (8.b)$$

i.e. that $a_{NH}$ and $a_H$ are respectively fixed at a given composition of the gas mixture, which defines $a_{NH}$ and $a_H$. If now (4) determines the rate according to (II), so that (3) is kept in equilibrium, we have further

$$a_{NH} = a_N a_H$$

or according to (8)

$$a_N = a_{NH} / a_{H}^{3/2} \tag{9.a}$$

In the case of the rate-determining step of (3), when $a_N a_H$ is definitely smaller than $a_{NH}$, we have

$$a_N < a_{NH} / a_{H}^{3/2} \tag{9.b}$$

instead. Eq. (9) states that $a_{NH} / a_{H}^{3/2}$ is the upper limit to $a_N$ in general and is approached by $a_N$ particularly as (4) controls the rate, or in other words, that $a_N$ depends not only on the composition of the gas mixture around, which defines $a_{NH} / a_{H}^{3/2}$, but also on the history of the catalyst's surface which decides the rate-determining step by (II). The $a_N$, thus determined kinetically by the surface state of the catalyst, reciprocally conditions the latter, giving rise to the stable hysteresis as illustrated in what follows.

§ 3 Phase Equilibria

Fig. 2 reproduces the experimental results of Emmett and col-
labrators, Paranjpe and collaborators and Burdese by the plot of the ammonia percent in ammonia-hydrogen mixture at 1 atm total pressure, which is in equilibrium with the solid phase formed from pure iron and the same gas mixture, against the nitrogen content in the solid phase in weight percent of nitrogen or in the corresponding atomic ratio of nitrogen to iron. The height of the horizontal line gives the composition of the gas mixture at the equilibrium of the reaction

$$4\text{Fe} + \text{NH}_3 = \text{Fe}_3\text{N} + \frac{3}{2}\text{H}_2,$$

i.e. at that of α-phase (Fe) and γ'-phase (Fe₃N) or that at the similar equilibrium of γ'- and ε-phase. The ammonia percent at the equilibrium of (10) is interpolated from the observation of the equilibrium constant $P_{\text{NH}_3}/P_{\text{NH}_2}$ by Emmett or Lehrer respectively at 22.4 or 21.8%.

![Phase diagram of iron-nitrogen system](image-url)
for the temperature 487°C of the present observation, while that of the \( \tau' \), \( \varepsilon \)-equilibrium similarly from the observation by Emmett\(^5\) or Lehner\(^6\) respectively at 60.2 or 59.5%, where \( P_H \) or \( P_{NH} \), is the partial pressure of hydrogen or ammonia at the equilibrium.

The vertical chain line signified by \( \tau' \), \( a \) or \( \varepsilon \), \( \tau' \) in Fig. 1 indicates the value \( (N_H/N_A)_\sigma \) or \( (N_H/N_A)_\varepsilon \) of \( N_H/N_A \), respectively appropriate to the mean value of the above pair of the ammonia percents at the \( \tau' \), \( a \)- or \( \varepsilon \), \( \tau' \)- equilibrium. It is seen from the Figure that the hysteresis in question begins to appear, just as \( N_H/N_A \) passes \( (N_H/N_A)_\sigma \) from above to below, i.e. the stable phase changes from \( a \) to \( \tau' \).

§ 4 Explanation of Hysteresis

We consider first \( a \)- and \( \tau' \)-phase only, assuming as if \( \tau' \)-phase were the only nitride. At the equilibrium of (10) in particular, when \( a \)-phase coexists with \( \tau' \)-phase, we have according to (V) another equilibrium of the reaction

\[
4Fe + N(a) = Fe_N ,
\]
so that the particular value \( a_{N,\sigma} \) of \( a_N \) at the equilibrium of (11) is determined as\(^*)\)

\[
a_{N,\sigma} = (a_{NH}/a_{H}^2)_{\sigma} ,
\]
where suffix \( \sigma \) signifies the particular value at the equilibrium of (10), i.e. that at the point \( N_H/N_A = (N_H/N_A)_\sigma \). It follows from the phase equilibrium of (11) that the \( a \)- or \( \tau' \)-phase is stable respectively according as \( a_N \) is lower or higher than \( a_{N,\sigma} \).

Consider now the catalyst at the entrance of the bed, which is flown steadily with the inflow gas. The \( a_{NH}/a_{H}^2 \) of the inflow gas increases monotonously with decrease of \( N_H/N_A \), because of the proportionality of \( a_{NH} \) to \( N_A \) and that of \( a_H \) to \( N_H \), equaling \( a_{N,\sigma} \) by (12), when \( N_H/N_A = (N_H/N_A)_\sigma \). If (4) governs the rate, \( a_N \) equals \( a_{NH}/a_{H}^2 \) according to (9.a) and hence increases with decrease of \( N_H/N_A \), coinciding with \( a_{N,\sigma} \), when \( N_H/N_A = (N_H/N_A)_\sigma \). In the case of the rate-determining step of (3), \( a_N \) may remain lower than \( a_{N,\sigma} \) according to (9.b), even if its upper limit \( a_{NH}/a_{H}^2 \) exceeds \( a_{N,\sigma} \). By decreasing \( N_H/N_A \) in the latter case, however, \( a_N \) increases monotonously as seen from (5) written in

\(^*)\) We have from the equilibria of (10) and (11), \( a_{Fe} \cdot a_{NH,\sigma} = a_{Fe,\sigma} \cdot a_{NH}^2 \) and \( a_{Fe,\sigma} \cdot a_{N,\sigma} = a_{Fe} \cdot a_{N} \) in accordance with (6), and hence (12), where \( a_{Fe} \) and \( a_{Fe,\sigma} \) are absolute activities of the respective solid phases.

—155—
the form according to (8), as

$$a_{NH_{3}}/a_{H_{2}} = a_0 a_{NH_{3}^{2}} + k_0/k_1 a_{\lambda}^2,$$

(13)
even to exceed $a_{N_{\lambda}}$. The $a_{N}$ at the entrance increases thus monotonously with decrease of $N_{H}/N_{\lambda}$ and attains $a_{N_{\lambda}}$ or remains below it, when $N_{H}/N_{\lambda}$ just equals $(N_{H}/N_{\lambda})_b$ according as (4) or (3) determines the rate. 

We consider next the variation of $a_{N}$ along the flow through the catalyst's bed at the given $N_{H}/N_{\lambda}$ for a definite state of catalyst's surface throughout. The left of (13) decreases monotonously along the flow, since $a_{NH_{3}}$ decreases but $a_{H_{2}}$ increases, as NH$_3$ decomposes to yield H$_2$. The $k_2/k_1$, being definite for the definite state of the catalyst's surface, (13) states that $a_{N}$ decreases steadily along the flow in the catalyst's bed.

It follows from (a) and (3) that the catalyst's surface is secured definitely at the state of $a$-phase over the region, where $N_{H}/N_{\lambda} = (N_{H}/N_{\lambda})_b$ at the entrance of the catalyst's bed as well as at its interior.

Starting from the latter state, the $N_{H}/N_{\lambda}$ may be decreased to some extent below $(N_{H}/N_{\lambda})_b$ without causing $a_{N}$ to exceed $a_{N_{\lambda}}$, keeping the previous state stable throughout according to (a), until $a_{N_{\lambda}}$ is surpassed by $a_{N}$ first at the entrance to turn catalyst's surface there from $a$- into $r'$-phase. Even then the catalyst's surface in the interior of the bed may remain stably at the state of $a$-phase according to (3).

It follows besides from (IV), that the catalyst's surface at the entrance, if once turned into $r'$-phase, carries forward the gas mixture of greater $a_{NH_{3}}/a_{H_{2}}$ to farther portion of the catalyst along the flow to promote nitridation there. The catalyst is thus nitrided progressively from the entrance toward the exit along with the decrease of $N_{H}/N_{\lambda}$, resulting in the decrease of $R$ by (IV) below its value which would be maintained, if the catalyst's surface remained at the state of $a$-phase whole throughout.

Let a) or b) be the curve of $R$ versus $N_{H}/N_{\lambda}$, which would be realized when the catalyst's surface were at the state of $a$- or $r'$-phase respectively throughout. $R$ descends thus from the curve a) with decrease of $N_{H}/N_{\lambda}$, to the curve b), which lies below a) according to (IV). Let C be the point where $R$ just meets the curve b). Increasing now $N_{H}/N_{\lambda}$ from the value lower than that at C, $R$ does not trace its former course beyond C, because $a_{N}$ on $r'$-phase is kept according to (9.a) equal to $a_{NH_{3}}/a_{H_{2}}$, which is higher than at $(N_{H}/N_{\lambda})_b$ and hence sufficient to secure its present state of $r'$-phase stable. But since $a_{NH_{3}}/a_{H_{2}}$ at the entrance decreases with increase of $N_{H}/N_{\lambda}$ by (a) and $a_{NH_{3}}/a_{H_{2}}$ in the
interior of the catalyst’s bed decreases along the flow by \((\dot{\beta})\), a point must be arrived at with increase of \(N_{\text{H}}/N_{\text{A}}\), where \(a_{N} = a_{\text{NH}^{2}}/a_{\text{H}}^{2}\) decreases below \(a_{N,0}\), first at the exit to reduce nitride there to \(\alpha\)-phase and, with further increase of \(N_{\text{H}}/N_{\text{A}}\), the reduction propagates toward the entrance. The \(R\) deviates now from the curve b) more and more upwards with the progress of the reduction according to (IV), until it returns to the curve a) at a point A, where the reduction is just completed at the entrance, i.e. at the composition \((N_{\text{H}}/N_{\text{A}})_{0}\) of inflow gas, corresponding to the equilibrium of (10).

We now consider \(\varepsilon\)-phase in addition to \(\alpha\)- and \(\gamma'\)-phase. Since \(a_{N}\) is kept constantly at \(a_{\text{SN}}/a_{\text{H}}^{2}\) on \(\gamma'\) as well as on \(\varepsilon\)-phase according to (II) and (9. a), the catalyst’s surface is at the equilibrium, by (9. a) relevant to the composition of the gas mixture irrespective of the history. The transition from the curve b) to that appropriate to \(\varepsilon\)-phase or reverse should in consequence occur at \((N_{\text{H}}/N_{\text{A}})_{0}\), possibly with some rise or drop of \(R\) but without any stable hysteresis. Let b') be the \(R\) curve of nitrides consisting of b) and the curve of \(\varepsilon\)-phase thus conjugated. The foregoing argument for the curves a) and b) holds similarly with regard to the curves a) and b'), leading likewise to the necessary appearance of the stable hysteresis.

The above inference thus accounts for the observation, leading, on the one hand, to the attribution of the curves a) and b') respectively to those A'AB and ECD in Fig. 1, and requiring on the other hand, that the point A must lie on the vertical chain line \(\gamma',\ a\), where the inflow gas is just in the equilibrium of (10) at the entrance as mentioned above, and that the transition from the curve b') to a) must be accompanied, because of the reduction, by an excess outflow of total nitrogen over its inflow, in the form of ammonia or nitrogen or both. The first requirement is fulfilled as seen from Fig. 1, while the second one verified by the experimental fact stated in §1, that outflow rate of ammonia has exceeded its inflow rate, since the overall synthesis of ammonia is excluded thermodynamically at the present experimental condition.

§ 5 Discussion

1. The observed hysteresis has been accounted for on the basis of the postulates from (I) to (V) in §2, which leads to the conclusion (\(\dot{\beta}\), §4 that \(a_{N}\) decreases along the flow through the catalyst’s bed. This conflicts, however, with one of consequences of the previous paper\(^{b}\),
that \( N(a) \) is in equilibrium with gaseous nitrogen and hence its activity increases with increase of nitrogen along the flow. The conflict is reconciled by modifying the above postulates, which defines the mechanism. Revised postulates are that, in place of \((1)\), both the reactions on \( \alpha \)-phase and nitrides, follow the sequence \((2)\) whose third step is replaced by the two ones

\[
\text{NH}(a) \rightarrow \text{N}(F) + \text{H}(a), \quad (14.\ a)
\]

and

\[
\text{N}(F) \rightarrow \text{N}(a), \quad (14.\ b)
\]

that, instead of \((\text{II})\), \((14.\ a)\) is the rate-determining step on \( \alpha \)-phase and either \((14.\ b)\) or \((4)\) is that on nitrides, that, rather than \((\text{III})\), the backward rate of \((14.\ b)\) is negligible compared with its forward rate, and that, for \((\text{IV})\), the steady rate is smaller when governed by \((14.\ b)\) or \((4)\) than by \((14.\ a)\), while \((V)\) is eliminated. We have thus instead of \((5)\)

\[
V = k_1(a_{NH} - a_{N2}a_H) = k_2a_N,
\]

where \(a_N\) denotes the absolute activity of \(N(F)\). The experimental results are quite similarly explained as in the foregoing section on the basis of the modified mechanism defined by the new postulates without conflicting with the above consequence of the previous paper. The original and the modified mechanisms are compared schematically with special reference to the replaced steps, as

original modified

\[
\begin{align*}
\text{NH}(a) \rightarrow & \overset{\alpha}{} \text{N}(a) \rightarrow \overset{\gamma'}{N_2} \\
& \overset{\gamma}{N(F)} \quad \text{NH}(a) \rightarrow \overset{\alpha}{} \text{N}(F) \rightarrow \overset{\gamma}{\text{N}(a)} \rightarrow \overset{\gamma'}{N_2},
\end{align*}
\]

where \(\overset{\alpha}{}\) added to with \(\alpha\) or \(\gamma'\) denotes the rate-determining step on \(\alpha\)- or \(\gamma'\)-phase and \(\overset{\gamma}{}\rightarrow\) the equilibrium relation postulated by \((V)\).

The modified mechanism will be investigated further in later works.

2. Present experimental results exclude, as shown below, the recombination \(2\text{N}(a) \rightarrow \text{N}_2\) of adsorbed nitrogen atoms as the rate-determining step on \(\alpha\)-phase, whether the step constitutes the original sequence \((2)\) or the modified one, which step has hitherto been usually assumed to be rate-determining but recently negatived by the determination of the stoichiometric number of the rate-determining step.
Let the recombination be the rate-determining step on $\alpha$- as well as on $\gamma'$-phase. Eq. (9. a) holds then invariably irrespective of the state of the catalyst's surface for both the original and the modified sequence of steps mentioned above. The consequence is that the catalyst's surface turns quite reversibly from $\alpha$- to $\gamma'$-phase or conversely according as $a_N$ defined by (9. a) rises above or fall below $a_{N\alpha}$, leaving no possibility of hysteresis over the region of $N_H/N_A$ where $\gamma'$-phase exists in equilibrium with gas, in contradiction to the observation. The conclusion is quite the same if the reaction be governed on $\gamma'$-phase by (14. b) instead, in the case of the modified sequence.

Next, we consider the case when the reaction is governed by the recombination (4) on $\alpha$-phase but by any other step on $\gamma'$-phase, first on the basis of the original sequence. The absolute activity product of the initial complex of the rate-determining step must exceed that of the appropriate final complex, i.e. $a_{NH} > a_{N\alpha}$ for the rate-determining step of (3), which has led to (9. b). We have, however, invariably (9. b), as readily be shown, by assuming any of the remaining three steps of the scheme (2) other than (3) and (4) as the rate-determining one and hence by rewriting any one of equal signs of (7) into that $>$ of inequality.

If then, the catalyst's surface begins to turn into $\gamma'$- from $\alpha$-phase, as soon as $a_N$, which equals $a_{NH}/a_{H\alpha}^{1/2}$ on $\alpha$-phase according to the premise, increases above $a_{N\alpha}$. But since $\gamma'$-phase causes to depress $a_N$ below $a_{NH}/a_{H\alpha}^{1/2}$, so that $\alpha$-phase is recovered but it turns again into $\gamma'$-phase and so on. The catalyst's surface thus oscillates between the states of $\alpha$- and $\gamma'$-phase over a certain range of $a_{NH}/a_{H\alpha}^{1/2}$ or of $N_H/N_A$, where $a_{N\alpha}$ lies between $a_{NH}/a_{H\alpha}^{1/2}$ and the value of $a_N$ kinetically reduced below $a_{NH}/a_{H\alpha}^{1/2}$ on $\gamma'$-phase. The oscillation may be only microscopic to reveal macroscopically a steady state apparently observed. But then the effect of the history of the catalyst's surface is extinguished, never giving rise to any stable hysteresis over the $N_H/N_A$-region, where $\gamma'$-phase is in equilibrium with gas, in conflict with the observation.

Just the same consequence is arrived at on the basis of the modified sequence assuming that the rate-determining step is the recombination (4) on $\alpha$-phase but any step of the sequence other than (14. b) and (4) on $\gamma'$-phase. The final conclusion is that the recombination of nitrogen atoms can not be assumed as the rate-determining step on $\alpha$-phase without opposing the observation, whether based on the original or the modified sequence.
Summary

Hydrogen-ammonia mixture of different definite compositions was allowed to flow through a catalyst's bed used in the previous experiment (Ref. 2) at 487°C and 1 atm total pressure, and the resulting percent $R$ of ammonia decomposition at the steady state finally attained was observed similarly as in the previous experiment (loc. cit.), keeping the inflow rate $N_A$ of ammonia at 70 cc NTP min$^{-1}$ and successively increasing or decreasing that $N_H$ of hydrogen from one to the other observation. It was thus found that $R$ reveals a stable hysteresis.

The hysteresis was satisfactorily accounted for on the basis of a slight modification of the mechanism concluded in the foregoing paper (Ref. 1) and of the known phase equilibrium of iron-nitrogen system (Refs. 6, 7 and 9), and shown to defy the rate-determining step of the recombination of adsorbed nitrogen atoms in accordance with the conclusion of the previous works (Refs. 5 and 1).

Author's best thanks are due to the Grant in Aid for Fundamental Scientific Research of the Ministry of Education.

References

1) J. HORIUTI and I. TOYOSHIMA, this Journal 6, 68 (1958).
2) J. HORIUTI and I. TOYOSHIMA, this Journal 5, 129 (1957).
4) J. HORIUTI, this Journal 1, 8 (1948); 4, 55 (1955).
12) A. BURDESE, Metallurgia ital. 47, 357 (1955).