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<th>MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST:Ⅱ: Analysis of Experimental Results for the Rate-Determining Step</th>
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MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST

II: Analysis of Experimental Results for the Rate-Determining Step

By Juro HORIUTI and ISAMU TOYOSHIJA

(Received June 9, 1958)

ENOMOTO, KOBAYASHI and one of the present authors have previously determined the stoichiometric number\textsuperscript{**})\textsuperscript{1}-5 of the rate-determining step of the catalyzed decomposition or synthesis at 2, which confines the rate-determining step to the first three of the sequence of steps

\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_2(a) + \text{H}(a), & 2 & \quad (1. I_a) \\
\text{NH}_2(a) & \rightarrow \text{NH}(a) + \text{H}(a), & 2 & \quad (1. I_b) \\
\text{NH}(a) & \rightarrow \text{N}(a) + \text{H}(a), & 2 & \quad (1. I_c) \\
2\text{H}(a) & \rightarrow \text{H}_2, & 3 & \quad (1. II_H) \\
2\text{N}(a) & \rightarrow \text{N}_2, & 1 & \quad (1. II_N)
\end{align*}

in so far as the decomposition

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

follows the sequence (1), where (a) signifies adsorbed atoms or atom groups and the annexed figure denotes the stoichiometric number\textsuperscript{**})\textsuperscript{1}-5 of the respective step.

Present authors have recently studied the catalyzed decomposition of ammonia, allowing 1:4 ammonia-hydrogen mixture to flow through a bed of doubly promoted synthetic catalyst of ammonia, measuring the outflow rate of undecomposed ammonia and analyzing the result

\textsuperscript{*)} J. H. and I. T.: Research Institute for Catalysis, Hokkaido University.

\textsuperscript{**) Number of times of a step to occur for every overall reaction specified by a definite chemical equation, as (2).
for the rate of catalyzed decomposition as a function of temperature and mol fraction of ammonia.

The above results are now statistical-mechanically analyzed to decide the rate-determining step among the above three, equally qualified to be, for having commonly the stoichiometric number 2.

§ 1. Experimental Results for Analysis

Table 1 shows the rate \( U \) of ammonia decomposition per second per gm catalyst (before reduction) as a function of ammonia mol fraction

<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( x )</th>
<th>0.183</th>
<th>0.172</th>
<th>0.150</th>
<th>0.135</th>
<th>0.133</th>
</tr>
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<tbody>
<tr>
<td>748</td>
<td></td>
<td>34.7</td>
<td>28.0</td>
<td>12.8</td>
<td>6.84</td>
<td>8.19</td>
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<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( x )</th>
<th>0.190</th>
<th>0.176</th>
<th>0.168</th>
<th>0.159</th>
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<tr>
<td>719</td>
<td></td>
<td>10.3</td>
<td>4.63</td>
<td>4.16</td>
<td>2.54</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( x )</th>
<th>0.176</th>
<th>0.145</th>
<th>0.121</th>
<th>0.098</th>
</tr>
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<tbody>
<tr>
<td>762</td>
<td></td>
<td>68.8</td>
<td>20.6</td>
<td>14.7</td>
<td>9.74</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( x )</th>
<th>0.145</th>
<th>0.113</th>
<th>0.090</th>
<th>0.061</th>
<th>0.060</th>
<th>0.032</th>
</tr>
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<tbody>
<tr>
<td>786</td>
<td></td>
<td>91.3</td>
<td>63.7</td>
<td>30.8</td>
<td>19.8</td>
<td>17.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( x )</th>
<th>0.107</th>
<th>0.068</th>
<th>0.024</th>
</tr>
</thead>
<tbody>
<tr>
<td>801</td>
<td></td>
<td>94.3</td>
<td>64.5</td>
<td>24.6</td>
</tr>
</tbody>
</table>

*) As 100.7 gm (before reduction) catalyst occupied 54.5 cc, \( U \) in the present unit is obtained by dividing that in the foregoing paper (Ref. 6) by a factor \( 60 \text{ sec} \times \frac{100.7 \text{ gm}}{54.5 \text{ cc}} = 110.9. \)
x and temperature \( T^\circ \text{K} \), as recalculated, for the sake of an expedient theoretical treatment, from the rate (mol NH\(_3\), min\(^{-1}\) cc\(^{-1}\) catalyst’s bed) given in the foregoing paper\(^6\).

It is deduced as shown in Appendixes I, II and III with regard to these experimental results that

(I) \( T \) or \( x \) in the bulk of gas mixture is practically identical respectively with that \( T_0 \) or \( x_0 \) at the surface of the catalyst on the basis of the model that the temperature or the ammonia mol fraction varies linearly with distance across the gas film of uniform thickness coherent to the catalyst without turbulence but is homogeneous outside, that

(II) the directly observable rate \( U \) is practically identical with the unidirectional forward rate \( \bar{U} \) of decomposition at the experimental condition in question, and that

(III) \( N(a) \) is the sole adsorptive at the above experimental condition which significantly affects the reaction rate.

On these basis the data are analyzed in subsequent sections.

§ 2. General Method for Deciding the Rate-Determining Step

The forward or the backward rate, \( \bar{v} \) or \( \bar{v} \) of a thermal step is expressed in general as\(^3\)

\[
\bar{v} = \xi \frac{kT}{h} \frac{p^*}{p^t}, \quad \bar{v} = \xi \frac{kT}{h} \frac{p^*}{p^F},
\]

where \( \xi \) is the transmission coefficient, \( h \) or \( k \) the Planck's or Boltzmann's constant and \( p^*, p^t \) and \( p^F \) the Boltzmann factors\(^*\).

\[
p^* = \exp(-\mu^*/RT), \quad R: \text{gas constant}
\]

of the chemical potentials \( \mu^*, \mu^t \) and \( \mu^F \) of the critical complex \( * \); \( ** \), initial complex \( I \) and final complex \( F \) of the step, represented by \( \delta \). Developing \( p^* \) particularly for a heterogeneous step as \( *** \)

\[
p^* = G^{\delta} Q^*,
\]

we have for the forward rate of the rate-determining step of the

---

\(^3\) Cf. §8, Ref. 3.

\(^*\) The \( p^* \) or \( \mu^* \) is defined as that of a single critical complex existing in the system in question; it is not however meant with this definition that there should exist physically a single critical complex at a time in the system but that \( \bar{v} \) or \( \bar{v} \) in the system is physically reproduced by \( p^* \) or \( \mu^* \) of this definition.

\(^**\) Cf. §24, Ref. 3.
overall reaction in question

\[ \dot{v} = v \frac{kT}{h} G \theta_{\sigma^*(0)} \frac{q^*}{p^1}, \]  

(6, v)

with which \( U \) is given according to (II), § 1 as

\[ U = \bar{U} = \frac{\dot{v}}{v}, \]  

(6, U)

where \( v \) is the stoichiometric number of the rate-determining step, \( G \) is the number of sites \( \sigma^* \) for the critical complex allotted, in accordance with \( U \), to 1 gm catalyst before reduction, \( \theta_{\sigma^*(0)} \) the probability of a \( \sigma^* \) being empty, i.e. at the state capable of admitting a critical complex and \( q^* \) the BOLTZMANN factor of the reversible work \(^{**}\) required to assemble a critical complex in a preliminarily emptied, definite \( \sigma^* \), from its constituents in their respective standard states.

Different statistical-mechanical expression of \( U \) is obtained from (6) in terms of \( x \) and \( T \) and hence by (I), § 1, of \( x \) and \( T \) directly observed, depending on the step among the first three of (1) taken to be rate-determining. It is now the criterion for the valid rate-determining step that the appropriate statistical-mechanical expression, when fitted to the experimental results, gives reasonable values of constants \( G \) etc. comprised in the expression as adjustable parameters.

The rate is however modulated through the probability \( \theta_{\sigma^*(0)} \) in (6) by the adsorption on the catalyst's surface as formulated in the subsequent sections on the basis of (III), § 1.

§ 3. Adsorption in General

The probability \( \theta_{\sigma(a)} \) of an adsorptive \( \sigma(a) \) being situated in a site \( \sigma \) is given in general\(^{***}\), as

\[ \theta_{\sigma(a)} = q^\sigma(a) \theta_{\sigma(0)} / p^\sigma(a), \]  

(7)

where \( \theta_{\sigma(0)} \) is the probability of the site \( \sigma \) being empty, i.e. at the state capable of admitting \( \sigma(a) \), and \( q^\sigma(a) \) the BOLTZMANN factor of the reversible work to form \( \sigma(a) \) in a preliminarily emptied, definite site \( \sigma \) from its constituents in their respective standard states. Eq. (7) is

\(^{**}\) The work at the statistical-mechanical equilibrium with a definite composition of the whole system. Cf. § 7, Ref. 3.

\(^{***}\) Cf. § 5 and § 17, Ref. 2. Eq. (5) is the special case of (7) for the critical complex, when the probability \( \theta_{\sigma(a)} \) of finding a single critical complex [cf. Footnote \(^{**}\) on p. 70] in a site \( \sigma^* \) equals the reciprocal of the total number \( G \) of the kindred sites.
now transformed into the form accessible to the evaluation of $\theta_{\sigma(3)}/\theta_{\sigma(0)}$ as below.

The $q^{(\alpha)}_6$ in (7) is given, provided that modes of motion of $\alpha$ in $\sigma$ are exclusively vibrations, by the product of the appropriate vibrational partition functions and the Boltzmann factor of the energy $\varepsilon^{(\alpha)}$ of the ground state\(^*\), or simply by the latter factor alone as

$$q^{(\alpha)}_6 = \exp\left(-\frac{\varepsilon^{(\alpha)}_6}{RT}\right), \quad (8)$$

if the vibrational frequencies are respectively large enough.

The $p^{(\alpha)}_\delta$ in (7) may be expressed, in accordance with (4), by the appropriate $p^{(\delta)}_\delta$ of gaseous molecule $\delta(g)$, which is in preliminary equilibrium with $\delta(a)$; for the adsorption equilibrium

$$N_a(g) = 2N(a), \quad (9.e)$$

for instance, we have

$$p^{N_a(g)}_\delta = (p^{N(a)}_\delta)^2. \quad (9.p)$$

The $p^{(\delta)}_\delta$ is now given as\(^*\)

$$p^{(\delta)}_\delta = Q^{(\delta)}_\delta / N^{(\delta)}_\delta, \quad (10)$$

where $Q^{(\delta)}_\delta$ is the partition function of a single gas molecule $\delta(g)$ in unit volume and $N^{(\delta)}_\delta$ its concentration. For the adsorption equilibrium of (9.e) in particular, we have from (7), (9.p) and (10)

$$\theta_{\sigma(\alpha)}/\theta_{\sigma(0)} = q^{(\alpha)}(N^{N(a)/Q^{N(\delta)}_\delta)^{1/2}} \quad (11.a)$$

or referring to the relation $\theta_{\sigma(\alpha)} + \theta_{\sigma(0)} = 1$ valid in compliance with (III), § 1

$$\theta_{\sigma(0)} = \left\{1 + q^{(\alpha)}(N^{N(a)/Q^{N(\delta)}_\delta)^{1/2}} \right\}^{-1}. \quad (11.b)$$

The $Q^{(\delta)}_\delta$ is expressed for large vibrational frequencies as in the cases of NH\(_2\), N\(_2\), and H\(_2\), with a good approximation as

$$Q^{(\delta)}_\delta = Q^{(\delta)}_\delta \exp\left(-\varepsilon^{(\delta)} \varepsilon^{(\delta)}/RT\right), \quad (12.Q)$$

where

$$Q^{(\delta)}_\delta = \frac{(2\pi m^2kT)^{3/2}}{h^3} \frac{8\pi^2 I^3 kT}{\varepsilon^3 h^2} \quad (12.L)$$

for a linear, inclusive of diatomic, molecule or as


\(^*\) Cf. § 5, Ref. 3.
Mechanism of Catalyzed Decomposition of Ammonia II

\[ Q_g^{(g)} = \frac{(2\pi m^3 kT)^{\frac{3}{2}}}{h^3} \]
\[ \frac{8\pi^4 (2\pi I^5 kT)^{\frac{3}{2}}}{8^3 h^3} \]  
\hspace{1cm} (12. C)

for a nonlinear molecule; \( m \) is the mass of \( \delta(g) \), \( I^3 \) the moment of inertia for a linear, inclusive of diatomic, molecule or the geometric mean of the three principal moments of inertia for a nonlinear molecule, \( s^3 \) the symmetry number and \( \varepsilon^{3(g)} \) the energy of the ground state.

\[ I^H_1 = 0.460^{\circ}, \quad I^N_x = 13.9^{\circ}, \quad (12. H_2), (12. N_2) \]
\[ I^H_1 = 4.44^{\circ}, \quad I^N_3 = 2.82^{\circ}. \quad (12. A), (12. BC) \]

We have now from (8), (11) and (12. \( Q \))

\[ \frac{\theta_{\sigma(N_2)}/\theta_{\sigma(g)}}{\left(\frac{N^{N_2}(g)}{Q^{N_2}(g)}\right)^{\frac{1}{2}}} \exp\left[\left(\varepsilon^{N_2(g)/2} - \varepsilon^{N_2(a)}\right)/RT\right] \]  
\hspace{1cm} (13. a)

and

\[ \frac{\theta_{\sigma(g)}}{\left(1+(N^{N_2(g)/Q^{N_2}(g)})^{\frac{1}{2}}\exp(\varepsilon^{N_2(g)/2} - \varepsilon^{N_2(a)})/RT\right)^{-1}} \]  
\hspace{1cm} (13. b)

The \( \varepsilon^{3(g)} \) in (12. \( Q \)) or \( \varepsilon^{3(a)} \) in (8) is combined with the respective partial molal enthalpy \( \bar{X}^{3(g)}_\rho \) or \( \bar{X}^{3(a)}_\rho \) as

\[ \varepsilon^{3(g)} = \bar{X}^{3(g)}_\rho - \frac{n^{3(g)}}{2} RT, \quad \varepsilon^{3(a)} = \bar{X}^{3(a)}_\rho, \]  
\hspace{1cm} (14. g), (14. a)

where \( n^{3(g)} \) is 7 or 8, according as \( \delta(g) \) is linear (inclusive of diatomic) or nonlinear, and the (differential) heat of adsorption is given by the excess of \( \bar{X}^{3(g)}_\rho \) over the total sum of partial molal enthalpies of adsorptives formed from \( \delta(g) \). The heat \( \Delta X(N_2) \) of dissociative adsorption of nitrogen is thus given as

\[ \Delta X(N_2) = \bar{X}^{N_2(g)}_\rho - 2\bar{X}^{N_2(a)}_\rho = \varepsilon^{N_2(g)} - 2\varepsilon^{N_2(a)} + \frac{7}{2} RT. \]  
\hspace{1cm} (15)

The \( \frac{\theta_{\sigma(N_2)}/\theta_{\sigma(g)}}{\theta_{\sigma(a)}} \) and the relevant \( \theta_{\sigma(a)} \) for instance are thus evaluated by (13), (12. L), (12. N_2) and (15) from the knowledge of \( \Delta X(N_2) \).

\( \)*) We have

\[ \bar{X}^3_\rho = RT^2 \alpha \ln p^7/\beta T \]

from (4) and the thermodynamical relation \( \bar{X}^3_\rho = \mu^3 - T\beta^3/\theta T \), where the partial differential coefficients refer to the fixed constituents and the fixed total pressure of the system in question. Eq. (14. g) follows from the above equation, (10) and (12), inasmuch as \( kT \Delta N^{3(g)} = p^3 \) and the partial pressure \( P^5 \) of \( \delta(g) \) is constant at fixed constituents and total pressure. Eq. (14. a) is derived from the above equation, (7) and (8), under the condition that \( \theta_{\sigma, \delta}/\theta_{\sigma(g)} \) is constant at the fixed constituents of adsorptive and total pressure.
§ 4. Decision of the Rate-Determining Step

The \( p' \) in (6. \( \bar{v} \)) is expressed for the respective cases when the rate-determining step is (1.I\(_a\)), (1.I\(_b\)) and (1.I\(_c\)), as\( ^*\)
\[
p' = p^{NH}_A, \quad p^{NH}_A/(p^{H}_A)^{1/2}, \quad p^{NH}_A/p^{H}_A. \quad (16. \text{I}_a), (16. \text{I}_b), (16. \text{I}_c)
\]

\( U \) is developed first for the rate-determining step (1.I\(_c\)) according to (6), (16.I\(_c\)) and (10) noting \( \nu = 2 \) and admitting that \( \kappa = 1 \), as
\[
U = \frac{kT}{2h} G \Theta_{\sigma(N)} q_{\sigma(N)}^{0} \frac{N^{NH}(e)Q^{H}(e)}{Q^{NH}(e)Q^{H}(e)}.
\]

(17. \( U \))

The \( \Theta_{\sigma(N)} \) is expressed in accordance with (11.b) assuming that \( \sigma^* \) consists of two adsorption sites \( \sigma^* \)'s each for \( N(a) \), as\( **\)
\[
\Theta_{\sigma(N)} = \Theta_{\sigma(N)}^2 = \left[1 + q^{N(a)}(N^{N}(e)/Q^{N}(e)^2)^{1/2}\right]^{-2}
\]

(17. \( \Theta \))

In the case when \( \sigma^* = \sigma \) i.e. \( \sigma^* \) consists of a single site \( \sigma \) of adsorption of \( N(a) \), the exponent to the second or the third member of the above equation is 1 or \(-1\) instead respectively. \( N^{N}(e)'s \) in (17) are expressed in the present case of the reactant gas of 1:4 ammonia-hydrogen mixture, in terms of the mol fraction \( x \) of ammonia as\( ***\)
\[
N^{NH}(e) = N, \quad N^{NH}(e) = \frac{N}{12}(11-7x), \quad N^{N}(e) = \frac{N}{12}(1-5x), \quad (18. NH_3), (18. H_2), (18. N_2)
\]

\( ^* \) Because of equilibria of steps other than the rate-determining one, e.g. of (1.I\(_c\)), we have similarly as (9.p), \( p^{NH}(e) = p^{NH}(e)N^{H}(e), p^{NH}(e) = p^{NH}(e)N^{H}(e) \) and \( p^{NH}(e)N^{H}(e) = p^{NH}(e)N^{H}(e) \), and hence \( p' = p^{NH}(e) = p^{NH}(e)/p^{H}(e) \), i.e. (16.I\(_c\)). Eq. (16.I\(_b\)) for \( p' = p^{NH}(e) \) is similarly derived, while (16.I\(_c\)) is self-evident.

\( ** \) The \( \Theta_{\sigma(N)} \) equals the square of \( \Theta_{\sigma(N)} \), provided that the probability \( \Theta_{\sigma(N)} \) of the site \( \sigma \) being empty is independent of the state, occupied or empty, of neighbouring sites, which is the case when any adsorptive exerts no force upon those in neighbouring sites.

\( *** \) Rates in the Table 1 are those of the gas mixture, whose mol fraction of each component respectively equals its fraction of flow rate (cf. Ref. 6). Let \( n^N, n^H, n^H \) be flow rates respectively of ammonia, nitrogen and hydrogen and \( n^N, n^H \) the values of \( n^N \) and \( n^H \) in the inflow gas. Fractions \( y^A, y^N, y^H \) etc. of flow rates of ammonia etc. are
\[
y^N = \frac{n^N}{n^A + n^H + n^N}, \quad y^H = \frac{n^H}{n^A + n^H + n^N}, \quad y^N = \frac{n^N}{n^A + n^H + n^N},
\]
while we have by the stoichiometry of (2) and the experimental condition
\[
\frac{n^N - n^A}{2} = \frac{n^H - n^H}{3} = n^N, \quad \frac{n^H}{n^A} = 4.
\]
Eliminating \( n^A, n^H, n^N, \) and \( n^N/n^A \) from the above six equations, we have
\[
y^H = \frac{11-7y^A}{12}, \quad y^N = \frac{1-5y^A}{12}
\]
or (18) in the text, identifying fractions of flow rates \( y^A \) etc. respectively with the appropriate mol fractions.
where \( N \) is the total concentration of gas mixture, which is constant throughout at constant temperature according to the present experimental condition.

We have now from (17) and (18)

\[
\left\{ \frac{x}{(11-7x)U} \right\}^{1/2} = \left( \frac{kT}{2h} \right) \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left\{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right\}^{1/2} \left( 1 - 5x \right)^{1/2},
\]

i.e. a linear relation between \( \{x/(11-7x)U\}^{1/2} \) and \( (1-5x)^{1/2} \) at constant temperature. Similar linear relations are derived for other combinations of the three cases of rate-determining step and the two cases of \( \sigma* \), as summarized by the equation

\[
F(x, U) = A \left\{ 1 + q^{N(x)} \left( N/12Q_{N(x)} \right)^{1/2} (1-5x)^{1/2} \right\} ;
\]

the function \( F(x, U) \) of \( x \) and \( U \), and constant \( A \) depends on the rate-determining step and \( \sigma* \) as shown in Table 2, where \( n \) is 2 or 1 according as \( \sigma* \equiv 2\sigma \) or \( \sigma* \equiv \sigma \).

**Table 2.** \( F(x, U) \) and \( A \) of the linear relation (20)

<table>
<thead>
<tr>
<th>Rate-determining step</th>
<th>( F(x, U) )</th>
<th>( A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_a ) ( \frac{x}{(11-7x)U} )(^{1/2} )</td>
<td>( \left( \frac{kT}{2h} \right) \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
<td>( \left( \frac{kT}{2h} \right) \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
</tr>
<tr>
<td>( I_b ) ( {x/(11-7x)}^{1/2}U )</td>
<td>( {kT/2h } \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
<td>( {kT/2h } \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
</tr>
<tr>
<td>( I_c ) ( {x/(11-7x) U }^{1/2} )</td>
<td>( {kT/2h } \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
<td>( {kT/2h } \frac{Gq^{\alpha(x)}}{Q_{\text{NH}2(x)}} \times \left{ 1 + q^{N(x)} \left( \frac{N}{12Q_{N(x)}} \right)^{1/2} \right}^{1/2} \left( 1 - 5x \right)^{1/2} ) ( -1/n )</td>
</tr>
</tbody>
</table>

Fig. 1 and 2 show respectively the linear relation of (19) and that of the same rate-determining step but of \( \sigma* \equiv \sigma \), i.e. that between \( x/(11-7x)U \) and \( (1-5x)^{1/2} \) as seen from (20) and Table 2. The linear relation (19) for \( \sigma* \equiv 2\sigma \) is satisfactorily obeyed, whereas that of the same rate-determining step for \( \sigma* \equiv \sigma \) yields negative \( A \), which is devoid of any physical meaning, besides that the appropriate linear relation is rather poor. As the same is true with the other two cases of \( \sigma* \equiv \sigma \), this sort of \( \sigma* \) is altogether excluded.

We deduce now values of the number \( G_i \) of \( \sigma* \) per unit area of the catalyst, i.e.
Fig. 1 Linear relation between $x/(1 - 7x)U^{1/2}$ and $(1 - 5x)^{1/2}$.

$$G_1 = G/S,$$  \hspace{1cm} (21. G)

as well as $\varepsilon^{N(x)/2} - \varepsilon^{N(x)}$ and $Q^{N(x)}$, from $A$ and the inclination $q^{N(x)}(N/12Q^{N(x)} + y)^{1/2}$ of $F/A$ against $(1 - 5x)^{1/2}$, for deciding the valid rate-determining step, where $S$ is the surface area of the catalyst at the working state per 1 gm unreduced catalyst, i.e.

$$S = 1.3 \times 10^2 \text{ cm}^2/\text{gm},$$  \hspace{1cm} (21. S)

The $A$ of the rate-determining step (1. I) with $\sigma^* = 2\sigma$ is given according to Table 2, (21.G), (8) and (12.Q), as

$$A = \left( \frac{SKT}{2h} G_1 \frac{12Q^{N(x)}}{Q_0^{NH/(x)}} \exp \left( - \frac{\varepsilon^{*}(\text{H}) + \varepsilon^{H_2(x)} - \varepsilon^{NH_2(x)}}{RT} \right) \right)^{1/2},$$  \hspace{1cm} (22)

which states that $\log A$ is the linear function of $1/T$ with two unknown
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Fig. 2 Linear relation between $\frac{x}{11-7x}U$ and $(1-5x)^{1/2}$.

constants, log $G$, and $\varepsilon^{(I_e)} + \varepsilon^{H_2(g)} - \varepsilon^{NH_3(g)}$, provided that $Q_e^{H_2(g)}$ and $Q_e^{NH_3(g)}$ are spectroscopically evaluated by (12). The two unknowns are now fitted, by the method of least squares, to the values of log $A$ determined graphically from Fig. 1, as given in Table 3 with mean errors derived from deviations, taken as accidental errors, of log $A$ from the above relation. The smallest mean errors of log $G$, for the rate-determining step of $I_e$ indicate that the linear relation best fits in with this case.

The inclination $I(F/A)$ of $F'/A$ against $(1-5x)^{1/2}$ is developed on the other hand according to (20), (8) and (12), as
I(F/A) = \left( N_m / 12Q_{d,m}^{N_2} \right)^{1/2} \left( T_m / T \right)^{1/4} \exp \left\{ \left( \epsilon_{N^2} - \epsilon^N \right) / RT \right\}, \quad (23)

Table 3

<table>
<thead>
<tr>
<th>Rate-Determining Step</th>
<th>\log_{10} G_1</th>
<th>\log_{10} Q_{d}^{N_2} at 760°K</th>
<th>Heat of Adsorption of Nitrogen \Delta X(N_2) Kcal mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH_3 \rightarrow NH_2(a) + H(a)</td>
<td>24.5±1.3</td>
<td>25±3</td>
<td>36.8±11.6</td>
</tr>
<tr>
<td>NH_2(a) \rightarrow NH(a) + H(a)</td>
<td>18.5±0.8</td>
<td>27±2</td>
<td>43.5±7.8</td>
</tr>
<tr>
<td>NH(a) \rightarrow N(a) + H(a)</td>
<td>16.1±0.6</td>
<td>25±3</td>
<td>36.6±8.6</td>
</tr>
</tbody>
</table>

where \( N_m \) or \( Q_{d,m}^{N_2} \) is the constant value respectively of \( N \) or \( Q_{d}^{N_2} \) at an optionally adopted constant temperature \( T_m \), say the intermediate temperature 760°K of the experiments in question; the variable factor \( (T_m / T)^{1/4} \) allows for the proportionality of \( N \) to \( T^{-1} \) and for that of \( Q_{d}^{N_2} \) to \( T^{1/2} \). The \( \log Q_{d}^{N_2} \) and \( \epsilon_{N^2} - \epsilon^N \) are similarly adjusted in accordance with (23) to the values of \( I(F/A) \) graphically evaluated at different temperatures; last two columns of Table 3 show \( \log Q_{d}^{N_2} \) and \( \epsilon_{N^2} / 2 - \epsilon^N \) thus determined with mean errors, the latter however in terms of \( \Delta X(N_2) \) around 760°K according to (15). It is to be noted that this value of \( Q_{d}^{N_2} \) is derived purely from kinetic data aside from its proportionality to \( T^{1/2} \) admitted above. With this kinetic value is to be compared the spectroscopic value \( Q_{d}^{N_2} = 10^{25} \). The heat \( \Delta X(N_2) \) of adsorption on the ammonia synthetic catalyst is 35.2 Kcal at 0.12 coverage or 37.0 Kcal at 0.19 coverage as determined in Appendix III respectively from the experimental result of KwA or that of Scholten and Zwetering, both in which cases \( \Delta X(N_2) \) varies with coverage. Brunauer and Emmett obtained practically constant value 35.0 Kcal over a range of adsorbed quantity from 2.6 to 3.6 cc NTP nitrogen on 18.3 gm Fe-Al_2O_3 catalyst as well as on 17.4 gm Fe-catalyst.

We see from the Table that the result is compatible with the reasonable order of magnitude \( 10^{19} \) of \( G \), solely in the case of the rate-determining step (I.I) with \( \sigma^* = 2\sigma \). In the latter case, moreover, the observed value of \( \Delta X(N_2) \) as well as the spectroscopic value of \( Q_{d}^{N_2} \) is kinetically reproduced within the accuracy of these indirect estimation.

On this ground we conclude that the rate-determining step is (I.I) with \( \sigma^* = 2\sigma \), or the dissociation of adsorbed imino group NH(a), whose critical complex occupies two adsorption sites of nitrogen atoms.
Summary

The previous observation of the present authors [this Journal, 5, 120 (1957)] on the rate of catalyzed decomposition of ammonia

$$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$$

in 1:4 ammonia-hydrogen mixture at 1 atm total pressure allowed to flow through a bed of doubly promoted ammonia synthetic catalyst at temperatures from 440°C to 528°C, was analyzed for deciding the rate-determining step among the first three of the scheme, \(\text{NH}_3 \rightarrow \text{NH}_2(a) + \text{H}(a), \text{NH}_2(a) \rightarrow \text{NH}(a) + \text{H}(a), \text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a), 2\text{N}(a) \rightarrow \text{N}_2, 2\text{H}(a) \rightarrow \text{H}_2\) \([a]: \text{adsorbed state}]) \), which three are equally qualified as being the rate-determining step for having its stoichiometric number 2 as found, with reference to the above chemical equation, by \text{ENOMOTO, HONRIUTI and KOBAYASHI} [this Journal 2, 87 (1953); 3, 185 (1955)]. The conclusion was that the rate-determining step was the third one, i.e. \(\text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a)\), which was arrived at as follows.

The catalyzed decomposition rate was statistical-mechanically formulated according to the generalized theory of reaction rate [HONRIUTI, this Journal 1, 8 (1948)] as a function of ammonia mol fraction and temperature ignoring all adsorptives but \(\text{N}(a)\) as confirmed by analysis of experimental data of adsorption. The formula of the reaction rate thus obtained for each of the three possible rate-determining step was now fitted to the experimental results mentioned above with the adjustable parameters, i.e. the number \(G_i\) of sites \(\sigma^*\)'s for the critical complex of the rate-determining step per unit area of catalyst's surface, the partition function \(Q_{N_2}^{N^*}\) of gaseous nitrogen molecule and the heat \(\Delta X(N_2)\) of dissociative adsorption of nitrogen. The result, from which the above conclusion was deduced, was that the crystallographic \(G_i\) and spectroscopic \(Q_{N_2}^{N^*}\) respectively of the order of magnitude of \(10^6\) and \(10^7\) as well as the experimental value around 37 Kcal mol\(^{-1}\) of \(\Delta X(N_2)\) were reproduced from the above adjustment to kinetic data solely in the case when \(\text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a)\) was taken the rate-determining step with \(\sigma^*\) consisting of two adsorption sites \(\sigma\)'s each for a nitrogen atom adsorbed.

The present authors wish to thank Dr. T. NAKAMURA for his valuable advices; their thanks are also due to the Grant in Aid for Fundamental Scientific Research of the Ministry of Education.
Appendix I  Ammonia Mol Fraction and Temperature at the Catalyst's Surface.

In accordance with the model of the coherent gas film described in the text, we have at the steady state

\[ U = SDN \frac{x - x_0}{J} = \frac{S\tau}{q} \frac{T - T_0}{J}, \quad (i) \]

where \( x \) or \( T \) is the homogeneous mol fraction of ammonia or temperature in the surrounding gas phase, \( x_0 \) or \( T_0 \) that at the catalyst's surface, \( J \) the thickness of the gas film, \( S \) the area of the catalyst's surface per gm unreduced catalyst, \( D \) the diffusion constant of ammonia through the gas film, \( \tau \) its thermal conductivity and \( q \) the heat of reaction per mol ammonia decomposed. \( D \) is expressed as a function of concentrations \( N_{\text{NH}_3} \) etc. respectively of ammonia etc. as

\[ D = \frac{N_{\text{H}_2}(g)H_2 + N_{\text{N}_2}(g)N_2 + N_{\text{NH}_3}(g)NH_3}{3(N_{\text{NH}_3}(g) + N_{\text{NH}_3}(g))} \lambda_{\text{H}_2} \lambda_{\text{N}_2} \lambda_{\text{NH}_3}, \quad (ii) \]

where \( \lambda_{\text{H}_2} \), \( \lambda_{\text{N}_2} \) or \( \lambda_{\text{NH}_3} \) is the products of the mean velocity and the mean free path of \( \text{H}_2 \), \( \text{N}_2 \) or \( \text{NH}_3 \) in gas mixture respectively, which depends on the composition of gas besides on temperature. The \( \lambda^{3} = \bar{C}^{3} \bar{l}^{3} \) was determined by calculating the mean velocity \( \bar{C}^{3} \) from the molecular weight \( M^{3} \) as

\[ \bar{C}^{3} = (8RT/\pi M^{3})^{1/2} \]

and the mean free path \( \bar{l}^{3} \) by the equation

\[ Z^{3} = \frac{\lambda^{3}}{3} \frac{\partial N^{3}}{\partial z} + u N^{3}, \quad \bar{z} = \text{H}_2, \text{N}_2, \text{NH}_3, \]

where \( N^{3} \)'s are the concentrations \( N_{\text{H}_2}(g) \) etc., \( z \) the distance measured from the bulk toward the catalyst's surface along the normal to the latter and \( u \) the rate of mass motion which levels the inhomogeneity of total concentration caused by the several diffusions. The condition of the homogeneity thus maintained is

\[ \frac{\partial N_{\text{H}_2}(g)}{\partial z} + \frac{\partial N_{\text{N}_2}(g)}{\partial z} + \frac{\partial N_{\text{NH}_3}(g)}{\partial z} = 0, \]

while that of the steady state is

\[ \frac{Z_{\text{H}_2}}{3} = Z_{\text{N}_2} = - \frac{Z_{\text{NH}_3}}{2}. \]

Eliminating \( Z^{3}, Z_{\text{N}_2}, \frac{\partial N_{\text{H}_2}(g)}{\partial z}, \frac{\partial N_{\text{N}_2}(g)}{\partial z} \) and \( u \) from the above six equations, we have \( Z^{3} = -D \frac{\partial N_{\text{NH}_3}(g)}{\partial z} \), where \( D \) is given by (ii) in the text.
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\[ \hat{\delta}_2 = \left[ \pi \sum_i N_i^3/\sigma_{kl}^2 (1 + M_i^2/M_2^2)^{1/2} \right]^{-1} \]

used in the foregoing paper\(^6\), where \( \hat{\delta}_k \) or \( \hat{\delta}_l \) is \( k \)-th or \( l \)-th \( \hat{\delta} \), and \( \sigma_{kl} \) the mean of the collision diameters of \( \hat{\delta}_k \) and \( \hat{\delta}_l \). Substituting \( N_i^3 \)'s into (ii) from (18), \( D \) was calculated for \( x=0.1 \) and \( T=760^\circ \text{K} \), as

\[ D = 0.40 \text{ cm}^2 \text{ sec}^{-1} (x = 0.1, \ T = 760^\circ \text{K}). \quad \text{(iii)} \]

The thermal conductivity \( \gamma \) was calculated as

\[ \gamma = \gamma_{\text{NH}_3} \frac{N_{\text{NH}_3}(g)}{N} + \gamma_{\text{H}_2} \frac{N_{\text{H}_2}(g)}{N} + \gamma_{\text{N}_2} \frac{N_{\text{N}_2}(g)}{N} \quad \text{(iv)} \]

in accordance with the additivity\(^{13} \) experimentally verified with binary mixture, where \( \gamma_{\text{NH}_3} \), etc. are the thermal conductivities of pure \( \text{NH}_3 \), etc. respectively. The \( A \) was taken at 0.1 cm perhaps the upper bound.

On the base of numerical values, \( q=12.7 \) Kcal mol\(^{-1} \)\(^{\circ} \text{C} \), \( S=1.3 \times 10^5 \) cm\(^2\) gm\(^{-1} \) of (21.5), \( D=0.40 \text{ cm}^2 \text{ sec}^{-1} \) of (iii) and \( \gamma=7.3 \times 10^{-4} \) cal cm\(^{-1} \) sec\(^{-1} \) deg\(^{-1} \)\(^{\circ} \text{C} \) calculated by (iv) at \( x=0.1 \), the fractions \( (x-x_0)/x \) or \( (T-T_0)/T \) of the decreases of \( x \) or \( T \) across the gas film was worked out at the order of magnitude of \( 10^{-1} \) or \( 10^{-3} \) respectively at 760\(^\circ \text{K} \), from which it is concluded that the difference is altogether negligible or that \( x_0 \) and \( T_0 \) are respectively identifiable with \( x \) and \( T \).

Appendix II Practical Identity of \( U \) and \( \bar{U} \)

Directly observable rate \( U \) of a steady reaction is given by the excess of the forward rate \( \bar{v} \) over the backward one \( \bar{v} \) of the rate-determining step divided by its stoichiometric number \( \nu \), as

\[ U = \frac{\bar{v} - \bar{v}}{\nu} = \bar{U} \left( 1 - \frac{\bar{v}}{\bar{v}} \right), \]

where

\[ \bar{U} = \frac{\bar{v}}{\nu} \]

is defined as the forward unidirectional rate of the overall reaction. Substituting \( \bar{v} \) and \( \bar{v} \) from (3), we have according to (4)

\[ U = \bar{U} \left( 1 - \exp \left( \frac{\mu - \mu^1}{RT} \right) \right). \]

\(^{13} \) The \( \gamma_{\text{NH}_3} \), etc. have been extrapolated, using the linear relation of \( \log \gamma_{\text{NH}_3} \), etc. to the reciprocal absolute temperature, from data given by J. D'ANS and E. LAX, "Taschenbuch, Berlin, 1948, p. 1136."
The difference $\mu^F - \mu^I$, and the similar difference of any other step, are respectively zero or not according as the step is in equilibrium or not. Admitting that all steps involved in the overall reaction except the rate-determining step are practically in equilibrium at the steady state, it follows that the free energy increase $\Delta F$ appropriate to the overall reaction equals $\nu$ times $\mu^F - \mu^I$ of the rate-determining step in accordance with the definition of stoichiometric number and hence that

$$U = \tilde{U} \left[ 1 - \exp \left( -\frac{\Delta F}{\nu RT} \right) \right].$$

The free energy increase $\Delta F$ is now given with special reference to the reaction (2) in terms of chemical potentials $\mu^{NH}$ etc. of ammonia etc. as

$$\Delta F = \mu^N + 3\mu^{H2} - 2\mu^{NH},$$

while $\mu^{NH}$ etc. are developed as

$$\mu^S = \mu^I + RT \ln P^S,$$

where $\mu^S$ is the value of $\mu^I$ at $P^S = 1$. We have from the above three equations

$$U = \tilde{U} \left[ 1 - \left( \frac{P^{NH}(P^{H2})^3}{K(P^{NH})^2} \right)^{1/\nu} \right],$$

noting that the standard free energy decrease $2\mu^{NH} - 3\mu^{H2} - 3\mu^{NH}$ is expressed by the equilibrium constant $K_r = P^{NH}/(P^{H2})^3$ as $2\mu^{NH} - 3\mu^{H2} = RT \ln K_r$, where $P^{NH}$ etc. are the values of $P^{NH}$ etc. respectively at equilibrium, i.e. at $\Delta F = 0$.

The second term in the parentheses was evaluated according to the empirical equation of HABER

$$-\frac{1}{2} \log K_r = \frac{9591}{4.571T} - \frac{4.98}{1.985} \log T - 0.00046 \frac{T}{4.571} + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10$$

with special reference to the present experimental condition. The result was that the second term was 0.049 at most for the stoichiometric number 2 of the rate-determining step or $U$ was practically identical with the forward unidirectional rate $\tilde{U}$ throughout the experimental conditions of Table 1.
Appendix III Adsorptions

Adsorptions are investigated of ammonia and of intermediates involved in the Scheme (1), which modulates the rate through $\theta_{\sigma(N)}$ comprised in (6. v).

Adsorption of Ammonia. Dew and Taylor\(^{15}\) have calorimetrically observed the heat $\Delta X(NH_3)$ of adsorption of ammonia on iron as 16 Kcal at 0°C. Identifying this value with that on the ammonia synthetic catalyst and assuming ammonia is adsorbed without dissociation, we have

$$\Delta X(NH_3) = \varepsilon_{NH_3(N)} - \varepsilon_{NH_3(a)} + 4RT = 16 \text{ Kcal},$$

by (14), and

$$\frac{\theta_{\sigma(NH_3)}}{\theta_{\sigma(N)}} = \frac{N_{NH_3}}{Q_{NH_3}} \exp \left( \frac{\varepsilon_{NH_3(N)} - \varepsilon_{NH_3(a)}}{RT} \right),$$

according to (7), (8), (10), (12.Q) and the equilibrium condition $p_{NH_3(a)} = p_{NH_3(N)}$ similar to (9.p). The $\theta_{\sigma(NH_3)}/\theta_{\sigma(N)}$ is calculated by the above two equations and (12.C), (12.A) and (12.BC) as

$$\theta_{\sigma(NH_3)}/\theta_{\sigma(N)} = 4.8 \times 10^{-7}$$

at the lowest temperature 719°K and the highest ammonia partial pressure 0.2 atm throughout the experimental conditions of Table 1. As the value of $\theta_{\sigma(NH_3)}/\theta_{\sigma(N)}$ is still lower at higher temperatures and lower partial pressures of ammonia according to the above equation and $\theta_{\sigma(N)}$ is less than unity, the molecular adsorption of ammonia may practically be ignored.

Dissociative Adsorption of Nitrogen. The $\theta_{\sigma(N)}/\theta_{\sigma(N)}$ and the heat of adsorption are determined on the basis of observations referred to in the text at the lowest temperature 719°K and the highest nitrogen partial pressure 0.083 atm\(^{9}\) as follows; we have from (13.a) a relation between $\theta_{\sigma(N)}/\theta_{\sigma(N)}$ and $\varepsilon_{NH_3(N)} - \varepsilon_{NH_3(a)}$, with $Q_{NH_3(N)}$ spectroscopically evaluated by (12.L) and (12.N) at the experimental condition specified by temperature and nitrogen partial pressure. Another relation between the same quantities is provided by observations of $\Delta X(N_2)$ at different amounts of adsorption of pure nitrogen, since the former determines

\(^{9}\) The partial pressure of nitrogen attained at the complete decomposition of 1:4 ammonia-hydrogen mixture at 1 atm total pressure; cf. (18. N$_2$), which reads $N_{N_2} = N/12$ at $x=0$. 

\[ -83 - \]
\[ \varepsilon^{N(g)/2} - \varepsilon^{N(a)} \] by (15), while the latter is converted into \( \Theta_{\sigma(N)/\sigma(\theta)} \) on the base of the surface area (21.5) and the number \( 10^{15} \) by the order of magnitude, of surface atoms of the catalyst, each assumed to afford a site \( \sigma \) of adsorption for a nitrogen atom. Admitting the latter relation to hold irrespective of temperature and pressure, \( \Theta_{\sigma(N)/\sigma(\theta)} \) and \( \varepsilon^{N(g)/2} - \varepsilon^{N(a)} \) are determined by solving above two simultaneous relations, i.e. by locating the intersection of the two curves of the plots of \( \Theta_{\sigma(N)/\sigma(\theta)} \) against \( \varepsilon^{N(g)/2} - \varepsilon^{N(a)} \), as

\[
\Theta_{\sigma(N)/\sigma(\theta)} = 0.14 \quad \text{and} \quad \Delta X(N_2) = 35.2 \text{ Kcal}
\]

or as

\[
\Theta_{\sigma(N)/\sigma(\theta)} = 0.25 \quad \text{and} \quad \Delta X(N_2) = 37.0 \text{ Kcal}
\]

respectively on the base of Kwan's (9) or SCHOLTEN and Zwietering's (10) work at the condition specified above.

This result shows that the adsorption of nitrogen must be taken into account, although the above value of \( \varepsilon^{N(g)/2} - \varepsilon^{N(a)} \) is uppermost throughout the experimental conditions in question (3).

**Dissociative Adsorption of Hydrogen.** The dissociative adsorption of hydrogen was quite similarly treated as in the case of nitrogen on the base of the heat of adsorption observed by Kwan (3), which decreases, similarly as that of nitrogen, with increasing amount of adsorption (4).

It was thus found that

\[
\Theta_{\sigma(H)/\sigma(\theta)} = 2.3 \times 10^{-2}, \quad \Delta X(H_2) = 13.5 \text{ Kcal}
\]

at the lowest temperature 719°K and the highest hydrogen partial pressure 0.917 atm (4) throughout the experimental conditions of Table 1. As \( \Theta_{\sigma(H)/\sigma(\theta)} \) is still lower at higher temperatures and lower hydrogen partial pressures similarly as in the case of nitrogen, it is concluded that the adsorption of hydrogen is practically negligible.

*) Step (I. II N) determining the rate brings about the equilibrium, \( 2N(a) + H_2 \leftrightarrow 2NH_3 \), in which case \( \Theta_{\sigma(N)} \) is identical with that at the equilibrium of (2), unless affected by the interaction of \( N(a) \) with \( N_2(g) \). At the latter equilibrium of nitrogen with 1:4 ammonia-hydrogen mixture of 1 atm pressure, the nitrogen pressure amounts to 1430 atm at 719K and in consequence \( \Theta_{\sigma(N)} \) must be much higher. This case is excluded however in accordance with the introduction.

**) HARKNESS and EMMETT (17) have thermodynamically determined the heat of adsorption of hydrogen on ammonia synthetic catalyst at 8.5 Kcal from their isotherms.

**++) The partial pressure of hydrogen attained at the complete decomposition of 1:4 ammonia-hydrogen mixture at 1 atm total pressure.
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Adsorption of NH(a) and NH₂(a). Adsorption of the intermediates NH(a) and NH₂(a) at the steady state of reaction depends on the rate-determining step operating. If (I.a) determines the rate, while all other steps are in equilibrium, we have the equilibria of partial reactions

\[ \text{NH}_3 = \text{NH}_2(a) + \frac{1}{2} \text{H}_2 \]  
and

\[ \text{NH}_2 = \text{NH}(a) + \text{H}_2, \]  
whereas, if (I.b) does similarly, we have those

\[ \text{NH}_2(a) = \frac{1}{2} \text{N}_2 + \text{H}_2 \]  
and

\[ \text{NH}(a) = \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{H}_2. \]

If now (I.b) is similarly determining the rate, the equilibria of (i.NH₂) and (ii.NH) are attained as readily be shown.

According as the equilibria of (i) or (ii) are established, we have for \( p_{\text{NH}_2} \) and \( p_{\text{NH}} \) respectively

\[ p_{\text{NH}_2} = p_{\text{NH}}/p_{\text{H}_2}^{1/2}, \quad p_{\text{NH}} = p_{\text{NH}_2}/p_{\text{H}_2} \]  
and

\[ p_{\text{NH}_2} = (p_{\text{N}}^{1/2}p_{\text{H}_2})^{1/2}, \quad p_{\text{NH}} = (p_{\text{N}}^{1/2}p_{\text{H}_2})^{1/2}, \]  
where suffix L or R signifies the relevance to the equilibria (i) or (ii). In the case of (I.a) determining the rate, \( p_{\text{NH}_2} \) and \( p_{\text{NH}} \) are given by (iii.NH₂) or (iv.NH) respectively.

It follows from (iii) and (iv) that

\[ p_{\text{NH}_2}/p_{\text{NH}} = p_{\text{NH}_2}/p_{\text{NH}} = p_{\text{NH}_2}/(p_{\text{N}}^{1/2}p_{\text{H}_2})^{1/2}, \]  

The third member of the above equation is less than unity in accordance with (4) in so far as the decomposition proceeds steadily, i.e. \( p_{\text{NH}_2} \) or \( p_{\text{NH}} \) with suffix L is less than that with suffix R. Since \( \theta_{\sigma_0} \) is the greater, the smaller is the appropriate \( p_{\text{NH}_2} \), as seen from (7), the upper bound to \( \theta_{\sigma_0} \) is obtained by substituting \( p_{\text{NH}_2} \) in (7) from (iii). We have thus, referring to (8), (10) and (12.Q), for the upper bound

\[ \text{Cf. (4) and (9)}. \]
The energies $\varepsilon_{\text{XH}_2}$ and $\varepsilon_{\text{NH}_2}$ in (vi) are now estimated assuming the additivity of bond energies, that $\text{N(a)}$, $\text{NH(a)}$ and $\text{NH}_2(a)$ form respectively triple, double and single bonds with the adsorbent and that energies of double and triple bonds are respectively twice and thrice as large as the single bond energy. The $\varepsilon_{\text{N(a)}}$ or the triple bond energy is determined according to (15) from the value of $\Delta X(N)$ observed by Kwan, which increases with decreasing coverage, the highest value observed being 50 Kcal at 0.04 coverage around 690 K; substituting the above highest value for $\varepsilon_{\text{XH}_2}$ and the dissociation energy of nitrogen molecule 224.9 Kcal for $\varepsilon_{\text{NH}_2}$, we have

$$\varepsilon_{\text{N(a)}} = -135.1 \text{ Kcal}$$

and hence

$$\varepsilon_{\text{NH}_2(a)} = 1/3 \cdot \varepsilon_{\text{N(a)}} - 2D(\text{N}-\text{H}) = -228.6 \text{ Kcal}$$

and

$$\varepsilon_{\text{NH}_2(a)} = 2/3 \cdot \varepsilon_{\text{N(a)}} - D(\text{N}-\text{H}) = -181.8 \text{ Kcal}$$

where $D(\text{N}-\text{H}) = 91.8 \text{ Kcal}$ is the bond energy between N and H. Substituting $\varepsilon_{\text{NH}_2(a)}$ and $\varepsilon_{\text{NH}_2(a)}$ from (vii) and the values of dissociation energies $-\varepsilon_{\text{XH}_2(a)} = 275.4 \text{ Kcal}$ and $-\varepsilon_{\text{XH}_2(a)} = 103.2 \text{ Kcal}$ into (vi), we have according to (12),

$$\theta_{\sigma(\text{NH}_2)}/\theta_{\sigma(\text{XH}_2)} = 2.6 \times 10^{-5}, \quad \theta_{\sigma(\text{NH}_2)}/\theta_{\sigma(\text{XH}_2)} = 0.18,$$

at the lowest temperature 719 K and the smallest $p_{\text{NH}_2(a)}$ and $p_{\text{XH}_2(a)}$ of 1:4

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5) We have from the spectroscopic data

$$\Delta H = \frac{1}{2}N_2 + 112.5 \text{ Kcal}$$

and

$$\Delta H = \frac{1}{2}H_2 + 154.8 \text{ Kcal}$$

in terms of energy decrease rather than enthalpy decrease. Similar equation is obtained for the ammonia synthesis reaction from the thermochemical observation of Haber (14) around 770 K according to (14, g) as

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = \text{NH}_3 + 12.7 \text{ Kcal} - 3RT = \text{NH}_3 + 8.1 \text{ Kcal}.$$

and hence we have

$$N + 3H = \text{NH}_3 + 275.4 \text{ kcal},$$

or the value of $D(\text{N}-\text{H})$ in question.
ammonia-hydrogen mixture under the experimental condition of Table 1. The upper bound of \( \frac{\theta_{\text{NH}_2}}{\theta_{\text{H}_2}} \) or \( \frac{\theta_{\text{NH}_3}}{\theta_{\text{H}_2}} \) given by (vi) is lower than the above value at other conditions of the experiments and moreover calculated even lower by taking smaller value of \( JX(N) \) than the above highest one as well as by allowing for the extra stability of the triple bond of nitrogen, i.e. that the triple bond energy is greater than the three halves of the double bond energy or three times the single bond energy \(^{15}\), which reveals itself distinctly in the case of \( \text{N}_2 \)-bond and even of \( \text{NC} \)-bond \(^{16}\).

On these grounds the adsorption of intermediates \( \text{NH}_2(a) \) and \( \text{NH}(a) \) is ignored under the experimental condition in question.

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