<table>
<thead>
<tr>
<th>Page</th>
<th>Instructions for use</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM</td>
</tr>
</tbody>
</table>

**Title**

EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM

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EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM

By

Koshiro Miyahara

(Received November 19, 1956)

§ 1. Introduction

Kemball has observed the rates of formation of different deuteromethanes from methane and deuterium on nickel and other metallic films and found that the initial rates of formation are of such relative magnitudes as \( \text{CH}_3\text{D} > \text{CH}_2\text{D}_2 > \text{CHD}_2 > \text{CD}_4 \) for all metals. He has also found that the activation energy of the initial formation of \( \text{CH}_3\text{D} \), e.g. on nickel, is 24 kcal, whereas those of \( \text{CH}_2\text{D}_2 \), \( \text{CHD}_2 \), and \( \text{CD}_4 \) on the same metal are commonly 31 kcal/mole. He concluded from these results that two kinds of reactions are going on, each forming \( \text{CH}_3\text{D} \) or the latter group of deuteromethanes.

In the present paper above experimental results are systematically deduced from the dissociative scheme,

\[
\begin{align*}
\text{I} & \quad \text{H}_2 \rightleftharpoons 2\text{H} \quad (a) \\
\text{II} & \quad \text{CH}_4 \rightleftharpoons \text{CH}_3\text{D} \quad (a) \quad \text{CH}_2\text{D}_2 \quad (a) \quad \text{CHD}_2 \quad (a) \quad \text{CD}_4 \quad (a)
\end{align*}
\]

where \( \text{H} \) stands for protium \( \text{P} \) and deuterium \( \text{D} \), and a few conclusions accessible to the experimental test inferred from the result of the analysis.

§ 2. Detailed Scheme and Qualitative Explanation

Scheme (1) may be developed discriminating between \( \text{P} \) and \( \text{D} \) as

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— 177 —
where the dotted or full line denotes the transfer of P or D respectively and the annexed number indicates the fraction of the rate of dissociation specified by the line, of the atom group on its left over the total rate of dissociation of the same atom group, identifying the kinetic behaviour of D with that of P.

On the basis of the Scheme (2) the Kempshall's experimental results at the initial stage of the reaction will first be qualitatively accounted for as follows, assuming that the overall equilibrium of the respective step is established, i.e. the overall forward and backward rates of each step are balanced with each other aside from the isotopic difference and that I and IIb among them are sufficiently quick that they are even isotopically in equilibrium.

The rate of formation of CPz(a) through III is large compared with those of CPzD(a), CPDz(a) and CDz(a), inasmuch as the concentrations of deuteromethanes are small compared with that of CPz at the initial stage of the reaction. Chemisorbed hydrogen atoms consist on the other hand practically exclusively of deuterium and CDz(a) must be much abundant compared with CPz(a) and CPD(a) on account of the isotopic equilibrium of I and IIb; the rates of formation of CPDz(a) and
lower substitution products through \( \text{H}_\text{II}_\text{a} \) are in consequence now negligibly small compared with that of \( \text{CD}_\text{III}_\text{a} \).

As the result both of the above situations \( \text{CP}_\text{II}_\text{a} \text{D}(\text{a}) \) and \( \text{CPD}_\text{II}_\text{a} \text{(a)} \) must be less abundant compared with \( \text{CP}_\text{III}_\text{a} \text{(a)} \) or \( \text{CD}_\text{III}_\text{a} \text{(a)} \). The rate of formation of \( \text{CP}_\text{II}_\text{a} \text{D}, \text{CPD}_\text{II}_\text{a}, \text{CPD}_\text{III}_\text{a}, \text{CD}_\text{III}_\text{a} \) is now given practically by that of combination of \( \text{D}(\text{a}) \) and \( \text{CP}_\text{II}_\text{a} \text{(a)} \) etc. respectively and hence the rates of formation of \( \text{CP}_\text{II}_\text{a} \text{D} \) and \( \text{CD}_\text{III}_\text{a} \) must be large compared with those of \( \text{CP}_\text{II}_\text{a} \text{D}_\text{II}_\text{a} \) and \( \text{CPD}_\text{III}_\text{a} \) at the initial stage of the exchange reaction as observed by Ke\( \text{m} \)ball. This qualitative explanation is now followed by detailed calculation adjusting the relative rates of each steps, assuming the isotopic equilibrium of \( \text{H}_\text{II}_\text{a} \) only but not that of \( \text{I} \).

### § 3. Calculation of the Fine Structure

The rate of formation of every atom group in the Scheme (2) is given as

\[
V^{\text{III}} = V(\text{III}) (y^\text{III}_p y^\text{III}_t - y^\text{III}_p) + V(\text{III}_a) (y^\text{III}_p y^\text{III}_t - y^\text{III}_t) + V(\text{II}_a) (y^\text{III}_t y^\text{III}_p - y^\text{III}_t) + V(\text{I}_a) (y^\text{III}_t y^\text{III}_p - y^\text{III}_t)
\]

\[
V^{\text{III}_a} = V(\text{III}) (y^\text{III}_p y^\text{III}_t + y^\text{III}_t y^\text{III}_p - y^\text{III}_p y^\text{III}_t) + V(\text{III}_a) (y^\text{III}_p y^\text{III}_t + y^\text{III}_t y^\text{III}_p - y^\text{III}_p y^\text{III}_t) + V(\text{II}_a) (y^\text{III}_t y^\text{III}_p + y^\text{III}_p y^\text{III}_t - y^\text{III}_t y^\text{III}_p) + V(\text{I}_a) (y^\text{III}_t y^\text{III}_p + y^\text{III}_p y^\text{III}_t - y^\text{III}_t y^\text{III}_p)
\]

\[
V^{\text{III}_t} = V(\text{III}) (y^\text{III}_t y^\text{III}_p + y^\text{III}_t y^\text{III}_p - y^\text{III}_t y^\text{III}_p) + V(\text{III}_a) (y^\text{III}_t y^\text{III}_p + y^\text{III}_t y^\text{III}_p - y^\text{III}_t y^\text{III}_p) + V(\text{II}_a) (y^\text{III}_t y^\text{III}_p + y^\text{III}_t y^\text{III}_p - y^\text{III}_t y^\text{III}_p) + V(\text{I}_a) (y^\text{III}_t y^\text{III}_p + y^\text{III}_t y^\text{III}_p - y^\text{III}_t y^\text{III}_p)
\]

and so on for \( V^{\text{III}} \) etc., \( V^{\text{III}_a} \) and \( V^{\text{III}_t} \) respectively, where \( V(j)(j=\text{I}, \text{II}_a, \text{or III}) \) denotes the overall forward or backward rate of the step \( j \) at overall equilibrium, and \( y^j \) the fraction of the number of \( \text{P}(\text{a}) \) over the sum of the numbers of \( \text{P}(\text{a}) \) and \( \text{D}(\text{a}) \), \( y^{\text{III}_t} \) the fraction of the
number of CP₄ over the sum of those of CP₃, CP₂D, CP₂D₂, CPD₃ and CD₄, and so on.

The \( y^{CP₃} \), \( y^{CP₂D} \) or \( y^{CD₄} \) may be expressed, because of the isotopic equilibrium of IIₐ, as

\[
y^{CP₃} = \left(y^{CP₄}\right)^2, \quad y^{CP₂D} = 2y^{CP₄}y^{P₄}, \quad y^{CD₄} = \left(y^{P₄}\right)^2. \tag{4}
\]

Specializing Eqs. (3.b) and (3.c) to the initial condition, i.e. \( y^{P₄} = y^{CP₃} = 1 \) and \( y^{P₄} = y^{CP₂D} = y^{CP₄} = \ldots = y^{CD₄} = 0 \), and putting rates \( V^{CP₄} \) etc. of intermediates CP₃(a) etc. individually zero for the steady state, we have

\[
V^{CP₃} = V(III)\left(1 - y^{P₄}\right)\left(1 - y^{P₄}\right)^2 = \frac{1}{1 - y^{P₄}}\tag{5.0}
\]

\[
V^{CP₂D} = V(III) ay^{P₄}\left(1 - y^{P₄}\right)^2 = \frac{1}{a} + 4\left(1 - y^{P₄}\right)^2\tag{5.1}
\]

\[
V^{CP₄,D₃} = 6V(III) a\left(y^{P₄}\right)^2\left(1 - y^{P₄}\right)^2\tag{5.2}
\]

\[
V^{CP₄,D₄} = 4V(III) a\left(y^{P₄}\right)^3\left(1 - y^{P₄}\right)^2\tag{5.3}
\]

\[
V^{CD₄} = V(III) a\left(y^{P₄}\right)^4\tag{5.4}
\]

where

\[
a = \frac{V(IIₐ)}{V(IIₐ) + V(III)} \tag{5. a}
\]

The values of \( a \) and \( y^{P₄} \) are adjusted according to the above equations to the experimental results of KEMBHALL at 6.4 mmHg partial pressures both of D₂ and CP₄. \( V^{CP₂D} \) etc. calculated from these values of \( a \) and \( y^{P₄} \) are in good agreement with observed values as shown in Table I.

The third last column of the Table shows the relative rate \( V(III)/V(IIₐ) \) calculated from \( a \) determined as above according to (5. a). The next column gives \( V(I)/V(IIₐ) \) calculated by equation

\[
V(I)/V(IIₐ) = y^{P₄}(1 - a)/(2a)(1 - y^{P₄}) \tag{6}
\]

which follows from (5. a), (4), the steady state equation for D(a) at the initial stage, i.e.

\[
y^{P₄}\left(2V(I) + V(IIₐ) + V(III)\right) = V(IIₐ)\left(\frac{1}{3}y^{CP₂D} + \frac{2}{3}y^{CD₄}\right) + 2V(I),
\]

those for CP₃D(a), CP₂D₂(a) and CD₄(a) obtained from last three equations of (3.c) putting the left side of each equal to zero and the relation, \( y^{P₄} + y^{P₄} = 1 \), by eliminating from these nine equations eight quantities

\( \text{*) The equation obtained similarly from the first of (3.c) is not linearly independent from these equations.} \)
Exchange Reaction Between Methane and Deuterium

i.e. $y^{p,P}$, $y^{p,D}$, $y^{C,D}$, $y^{P,D}$, $y^{C,D}$, $y^r$ and $V(III)/V(II_a)$.

§ 4. Discussion

1). It has been assumed in the qualitative explanation that the step I is practically in isotopic equilibrium and hence $y^D$ is nearly unity, whereas in the numerical calculation $y^D$ was not assumed unity but adjusted to the experiments. The result shown in Table I confirms this assumption in the qualitative explanation. The second term in the parenthesis of (5.1) is now negligible in accordance with this result.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temp. °C</th>
<th>Relative formation-rate of deuteromethane (%)</th>
<th>$\alpha$</th>
<th>$y^D$</th>
<th>$V(III)$</th>
<th>$V(II_a)$</th>
<th>$V(II_a)$</th>
<th>Slowest step</th>
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</thead>
<tbody>
<tr>
<td>Ni *)</td>
<td>228</td>
<td>obs. 13.2 2.2 20.3 64.4</td>
<td>0.865</td>
<td>0.925</td>
<td>0.156</td>
<td>1.800</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 13.0 2.6 19.5 64.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>obs. 10.2 2.3 20.4 67.6</td>
<td>0.900</td>
<td>0.925</td>
<td>0.111</td>
<td>1.302</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 9.6 2.6 20.4 66.4</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Rh</td>
<td>162</td>
<td>obs. 17 4 22 57</td>
<td>0.800</td>
<td>0.900</td>
<td>0.250</td>
<td>1.80</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 18.6 3.8 23.8 53.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>259.3</td>
<td>obs. 44 15 17 24</td>
<td>0.500</td>
<td>0.850</td>
<td>1.000</td>
<td>4.25</td>
<td>II_a = III</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 45.6 5.4 19.9 23.1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>W</td>
<td>150.6</td>
<td>obs. 72 3 11 14</td>
<td>0.250</td>
<td>0.830</td>
<td>2.770</td>
<td>8.75</td>
<td>II_a</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 70.8 3.6 11.5 14.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>254.3</td>
<td>obs. 94.6 1.3 2.0 2.0</td>
<td>0.040</td>
<td>0.800</td>
<td>24.00</td>
<td>49.92</td>
<td>II_a</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 95.2 0.8 2.0 2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni *)</td>
<td>341</td>
<td>obs. 5 5 20 70</td>
<td>0.956</td>
<td>0.925</td>
<td>0.046</td>
<td>0.555</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-calc. 3.9 2.8 22.9 70.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*) Reactions on this metal are of $P_{D_2} = 4.85$ and $P_{D_2} = 6.48$ mmHg.

2. It has been observed by KeMBHALI that the activation energy of the formation of $CP_2D_2$, $CPD_3$, or $CD_4$ on nickel is practically of a common value as mentioned above. It is concluded from this result in accordance with Eqs. (5.1), ... (5.4) that $y^D$ is a constant practically.
independent of temperature over its observed range; this conclusion
is in accordance with the results of analysis at 228°C and 255°C for
nickel as shown in Table I.

3. On the basis of the temperature independence of \( y^0 \) concluded
above the relative rates of formation of different deuteromethanes at
341°C are now calculated as below and compared with the experimental
results of Kemball.

The activation energies of the formation of \( \text{CP}_3\text{D} \) and \( \text{CP}_2\text{D}_2 \) are
expressed from Eqs. (5.1), (5.2) and (5.4) taking \( y^0 \) constant as

\[
\begin{align*}
E^{\text{CP}_3\text{D}} &= 2E(\text{III}) - E(\text{II}_a + \text{III}) \\
E^{\text{CP}_2\text{D}_2} &= E(\text{III}) + E(\text{II}_a) - E(\text{II}_a + \text{III}),
\end{align*}
\]

where \( E(\text{II}_a) \), \( E(\text{III}) \) or \( E(\text{II}_a + \text{III}) \) denotes the appropriate activation
energy, e.g. \( RT^2 \frac{d \ln V(\text{II}_a)}{dT} \), of \( V(\text{II}_a) \), \( V(\text{III}) \) or \( V(\text{II}_a + \text{III}) \) respectively. We have from the above relations and the observed values,
\( E^{\text{CP}_3\text{D}} = 24 \text{ kcal} \) and \( E^{\text{CP}_2\text{D}_2} = 31 \text{ kcal} \) mentioned in the introduction,

\[
E(\text{II}_a) - E(\text{III}) = 7 \text{ kcal}. \quad (7)
\]
on nickel, while the same quantity is given as 6.7 kcal from values of
\( V(\text{III})/V(\text{II}_a) \) at 228°C and 255°C on nickel in Table I in very satis-
factory agreement.

The values of \( V(\text{III})/V(\text{II}_a) \) on nickel at 341°C is now determined
from that at 228°C and (7) at 0.0427, from which we have \( a_{\text{III}} = 0.956 \)
according to (5.4). The \( V^{\text{CP}_3\text{D}} \) etc. at 341°C on nickel are now calculated
according to Eqs. (5.1), ...(5.4) for the same value of \( y^0 \) as that at 228°C,
i.e. 0.925, and compared with those observed by Kemball in the last
row of the Table I. The \( V(\text{IV})/V(\text{II}_a) \) in the Table is similarly calculated
according to Eq. (6). The calculation accounts for the experimental
result that the initial rates of formation are of the relative magnitudes,
\( V^{\text{CP}_3\text{D}} \approx V^{\text{CP}_2\text{D}_2} < V^{\text{CP}_1\text{D}} \),

The latter experimental result may be understood with reference
to the appreciable relative decay of \( V(\text{III}) \) from 228°C to 341°C as seen
in Table I, which upholds \( V^{\text{CP}_3\text{D}} \) as qualitatively stated in §2, rather
than by attributing to the difference of the evaporated films\(^1\).

4. The individual values of \( E(I) \) etc. on nickel are estimated as
below on the basis of the relative magnitudes of rates of formation
of deuteromethanes.

As \( y^0 \) on nickel is close to unity, \( V^{\text{IV}} \) may be identified with
Exchange Reaction Between Methane and Deuterium

\[ -V(\text{III}) \text{ neglecting the first two terms in the parenthesis } \{ \} \text{ of (5,0).} \]

We have hence

\[ E(\text{III}) = 30 \text{ kcal} \]

from the observed values of \( V^{\text{H}} \) at 255 °C and 214 °C, i.e., \(-0.3892\%\) and \(-0.0346\%\) respectively of total methane per min per mg of the metallic film. \( E(\text{II}_a) \) is now obtained from the above value of \( E(\text{III}) \) and (7) as

\[ E(\text{II}_a) = 37 \text{ kcal} \]

We have on the other hand from three values of \( V(\text{I})/V(\text{II}_a) \) at 228 °C, 255 °C and 341 °C given in Table I consistently

\[ E(\text{II}_a) - E(\text{I}) = 6 \text{ kcal}, \]

and hence

\[ E(\text{I}) = 31 \text{ kcal}. \]

This value of \( E(\text{I}) \) is considerably large compared with the value of the activation energy 13 kcal or 12 kcal of the chemisorption of hydrogen determined by the analysis of exchange reaction between hydrogen and water\(^{a}\) or ammonia\(^{b}\) respectively.

These values of \( E(\text{I}) \) etc. lead to a conclusion that the slowest step on nickel must be always \( V(\text{III}) \) even at sufficiently high temperature above those of Kemball's experiment.

5. The ratio of \( V^{\text{H}} \) and \( V^{\text{D}} \) is given by (3, a) as

\[ V^{\text{H}}: V^{\text{D}} = 2y^{\text{H}}(1-y^{\text{D}}) \]

for the initial stage where \( y^{\text{D}} = 1 \) and \( y^{\text{H}} = 0 \). Above equation shows that the direct determination of \( V^{\text{H}} \) \( V^{\text{D}} \) will check the value of \( y^{\text{D}} \) determined at present by analysis of the observation of \( V^{\text{H}}, V^{\text{D}} \) etc. It must be that \( V^{\text{H}} > V^{\text{D}} \) for all metals in Table I according to the equation above, since \( y^{\text{D}} \) is nearly unity at the initial conditions according to the analysis.

If the step I were slowest, \( y^{\text{D}} \) should approach zero as \( D(\alpha) \) supplied by the step is readily washed by protium from methane. In that case we have \( V^{\text{H}}<V^{\text{D}} \) on the contrary to the above and further according to Eqs. (5.0), \( \cdots (5.\alpha) \)

\[ V^{\text{H}}: V^{\text{D}}: V^{\text{HH}}: V^{\text{DD}} = 1: 4y^{\text{H}}: 6(y^{\text{D}})^2: 4(y^{\text{D}})^2: (y^{\text{D}})^3 \]

i.e. that the rate decreases monotonously along with increasing substitution with deuterium atoms.
Summary

1. The relative rates of formation of different deuteromethanes at the initial stage of the reaction observed by Kemball are satisfactorily explained by a reaction scheme consisting of the chemisorption of hydrogen and the successive dissociative chemisorption of methane molecule, and the results obtained are discussed especially for the case of nickel film.

2. The activation energy on nickel is determined as 31, 30 or 37 kcal for the step $H_{(a)} \rightarrow 2H_{(a)}$, $CH_{4(a)} \rightarrow CH_{2(a)} + H_{(a)}$ or $CH_{2(a)} \rightarrow CH_{2(a)} + H_{(a)}$ respectively.

3. It is concluded for the case of nickel that the fraction of the chemisorbed deuterium over the total chemisorbed hydrogen is a constant practically independent of temperature and that the slowest step must be always $CH_{4(a)} \rightarrow CH_{2(a)} + H_{(a)}$ even at sufficiently high temperature above those of Kemball’s experiment.

4. It is predicted that the initial rate of formation of PD must be larger than that of Pe for all metals observed by Kemball at his experimental conditions, but it must be the reverse in the case when the chemisorption of hydrogen is slowest.

5. The relative rates of formation of different deuteromethanes at the initial stage of the reaction are inferred for the case when the chemisorption of hydrogen is slowest.

The author wishes to express his sincere thanks to Professor J. Horiuti for his kind interest and valuable discussions on the present work and also to the Ministry of Education for the Grant for the Scientific Researches.

References