Title

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MECHANISM OF OXIDATION OF SULFUR DIOXIDE CATALYZED BY PLATINUM

By Makihiko Masuda* and Koshiro Miyahara*

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Abstract

It was found that the analysis made by Kaneko and Odanaka1,2) with regard to the mechanism of the reaction, 2SO₂ + O₂ = 2SO₃, catalyzed by platinum was not consistent in their application of the theory of the stoichiometric number3-5). Their experimental results were reexamined by considering the forward and the backward unidirectional rates of the oxygen transfers among O₂, SO₂ and SO₃. It was concluded that the sequence of steps, O₂ ←→ 2O(a), SO₂ ←→ SO₂(a) and SO₂(a) + O(a) ←→ SO₃, assumed by Kaneko and Odanaka is effective in a consistent interpretation of their experimental results, however, it results in conclusions that the first one of the above steps is the slowest and the last one nearly in equilibrium, running contrary to the conclusion of Kaneko and Odanaka that the last step is rate-determining.

§ 1. Introduction

The stoichiometric number, ν(r), of the rate-determining step, r, of an overall reaction is given by Horiuti3) as

ν(r) = -ΔG/RT ln(V+/V-)

and can be determined by observing the affinity, -ΔG, the steady rate, V(= V+ - V-), and the forward or the backward unidirectional rate, V+ or V-, respectively, of the overall reaction. Practically, V+ or V- is evaluated as a transfer rate of an isotope from a reactant to a resultant or the reverse, respectively, in the course of the overall reaction. Accordingly, ν(r) of Eq. (1) is often found to be infinitely large, as discussed by Frumkin6) and Matsuda and Horiuti4), in the case where the value of V+/V- is nearly unity on account of that the isotope used is exchanged through steps nearly equilibrated, other than r. Matsuda and Horiuti6) showed that the determination of a rate-determining step according to the theory of the stoichiometric number3) was made more reliable by taking account of a set

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of experimental values of $v(r)$, inclusive of infinitely large one, which can be obtained by introducing into Eq. (1) the value of $V_+/V_-$ observed by using isotopes of two or more elements involved in the overall reaction.

Kaneko and Odanaka\(^1\) (K.O. in what follows) have applied the theory of the stoichiometric number to the determination of the mechanism of oxidation of sulfur dioxide, catalyzed by platinum, using radioactive sulfur and heavy oxygen as isotopic tracers. They have observed the steady oxidation rate, as well as oxygen exchange rate\(^2\) between $O_2$ labelled by heavy oxygen and normal $SO_3$, and sulfur exchange rate\(^1\) between $SO_2$ labelled by radioactive sulfur and normal $SO_3$, and found both the values of $v(r)$ determined with heavy oxygen and radioactive sulfur to be ca. 2. K.O. have thus concluded that step $c$ of sequence (3) is the rate-determining one of reaction (2). Their conclusion is adequate only if sequence (3) assumed by them is correct and if $V_+$ and $V_-$ evaluated by them are the true unidirectional rates of reaction (2).

\begin{align*}
\text{a: } & O_2 \rightleftharpoons 2O(a), \\
\text{b: } & SO_2 \rightleftharpoons SO_2(a), \\
\text{c: } & SO_2(a) + O(a) \rightleftharpoons SO_3.
\end{align*}

(3)

The oxygen exchange can, however, take place in the course of reaction (2) not only between $O_2$ and $SO_3$ but also between $O_2$ and $SO_2$ or $SO_2$ and $SO_3$ as observed by K.O. themselves. This fact suggests the evaluation made by K.O. of $V_+/V_-$ to be erroneous. In the present paper the treatment of K.O. and their experimental results are reexamined in the light of a correct application of the theory of stoichiometric number.

§ 2. The results of the treatment of K.O. conflicting with each other.

As mentioned in Introduction, K.O. have determined the stoichiometric number of the rate-determining step of reaction (2) as ca. 2 according to Eq. (1) and their experimental results of oxygen exchange between $O_2$ and $SO_3$. They have evaluated then $V_+/V_-$ of Eq. (1) according to the equation,

\[ V_+/V_- = 1 + (z_{O_2} - z_{SO_3}) \frac{d \ln N_0}{dz_0}, \tag{4. R} \]

which was derived from the equations for mass balances that

\[ V = -dN_0/dt = V_+ - V_- \tag{4. V} \]
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and

\[-d (N_0 z_0)/dt = z_0, V_+ - z_{so}, V_-,\]

where \(N_0\) is the number of molecules of \(O_2\) in the reaction system and \(z_0\) or \(z_{so}\) the atomic fraction of heavy oxygen, \(O'\), in \(O_2\) or \(SO_3\), respectively. Provided that the above treatment of K.O. is valid, we alternatively have, with regard to the oxygen exchange between \(SO_2\) and \(SO_3\), the equations,

\[V = -dN_{so}/2 dt = V_+ - V_-\]

and

\[-d (N_{so}, z_{so})/dt = 2 z_{so}, V_+ - z_{so}, V_-\]

which result in

\[V_+/V_- = 1 + (z_{so} - z_{so}) d \ln N_{so}/dz_{so}.\]

Table 1 shows the experimental results of K.O. Also, in the last two columns are given the values of \(V_+/V_-\) evaluated from Eq. (5.R) and those of \(\nu(r)\) evaluated by introducing these values of \(V_+/V_-\) into Eq. (1). These values of \(\nu(r)\) are much larger than 2, and indicate, according to the view of K.O., that the main part of the oxygen exchange between \(SO_2\) and \(SO_3\) is caused by steps other than step c of sequence (3). Thus, it is inevitable to introduce a new step of formation of \(SO_3\) besides step c, which denies the validity of sequence (3).

**Table 1.** The experimental results of K.O. of oxidation of normal \(SO_2\) by \(O_2\) labelled by heavy oxygen over platinum catalyst and values of \(V_+/V_-\) and \(\nu(r)\) evaluated according to Eqs. (5.R) and (1), respectively.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time</th>
<th>(P_0) cmHg</th>
<th>(P_{so}) cmHg</th>
<th>(P_{so}) cmHg</th>
<th>(z_{o_1} \times 10^2)</th>
<th>(z_{so_3} \times 10^2)</th>
<th>(z_{so_2} \times 10^2)</th>
<th>(V_+/V_-)</th>
<th>(\nu(r))</th>
</tr>
</thead>
<tbody>
<tr>
<td>395</td>
<td>0 min</td>
<td>12.90</td>
<td>23.34</td>
<td>13.84</td>
<td>9.96</td>
<td>1.40</td>
<td>1.87</td>
<td>1.48</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>8.56</td>
<td>14.67</td>
<td>22.50</td>
<td>9.94</td>
<td>1.73</td>
<td>2.63</td>
<td>2.80</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>6.40</td>
<td>10.36</td>
<td>26.82</td>
<td>9.94</td>
<td>1.87</td>
<td>2.88</td>
<td>4.67</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>4.70</td>
<td>6.96</td>
<td>30.22</td>
<td>9.92</td>
<td>1.95</td>
<td>3.05</td>
<td>8.91</td>
<td>5.6</td>
</tr>
<tr>
<td>405</td>
<td>0 hr</td>
<td>8.16</td>
<td>16.87</td>
<td>7.42</td>
<td>11.02</td>
<td>1.64</td>
<td>2.43</td>
<td>1.43</td>
<td>47.7</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>6.71</td>
<td>13.96</td>
<td>10.33</td>
<td>11.00</td>
<td>1.93</td>
<td>2.84</td>
<td>1.75</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>4.53</td>
<td>9.59</td>
<td>14.70</td>
<td>10.97</td>
<td>2.26</td>
<td>3.35</td>
<td>2.88</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>7.92</td>
<td>1.97</td>
<td>4.49</td>
<td>19.80</td>
<td>10.80</td>
<td>2.52</td>
<td>3.73</td>
<td>7.74</td>
<td>5.3</td>
</tr>
</tbody>
</table>
§ 3. A general consideration of the unidirectional rates of oxygen transfer among $O_2$, $SO_2$, and $SO_3$.

The sequence of steps, (3), excludes a priori a chance of oxygen exchange between $O_2$ and $SO_2$ without passing through the step of $SO_3$-formation; such an exchange is called a direct exchange in what follows. It is easily seen that direct exchanges of oxygen among $O_2$, $SO_2$, and $SO_3$ are linearly independent of each other, as discussed in Appendix. To investigate the validity of sequence (3), let us start our general consideration from a sequence of steps, which causes an overall reaction,

$$\sum_{i=1}^{3} m_i M_i = 0, \quad (6)$$

and enables an isotope of an element, $A$, involved in all of the three species $M_i$'s, to be directly exchanged between any two of them. An example of such a sequence is provided by adding adsorbed sulfur trioxide, $SO_3(a)$, to sequence (3) as

$$\begin{align*}
a: & \quad O_2 \rightleftharpoons 2O(a), \\
b: & \quad SO_2 \rightleftharpoons SO_2(a), \\
c: & \quad SO_2(a)+O(a) \rightleftharpoons SO_3(a), \\
d: & \quad SO_3(a) \rightleftharpoons SO_3.
\end{align*} \quad (7)$$

Oxygen exchange between any two of $O_2$, $SO_2$, and $SO_3$ caused by these steps are direct, that is, linearly independent of each other as verified in Appendix. Reaction (6) is a generalized form of the present one, (2), as well as a large number of oxidations, hydrogenations etc. of a similar type, and, thus, their mechanisms can be analyzed in the same way as the present treatment.

With reference to reaction (6), we now define phenomenologically the forward or backward unidirectional rate, $V_{12}$ or $V_{21}$ respectively, of transfer of $A$ atoms from $M_1$ to $M_2$ through the path, $M_1-M_2$, of direct exchange of $A$ between $M_1$ and $M_2$ as follows.

We now denote the isotope of $A$ by $A'$. $V_{12}$ or $V_{13}$ is the rate of increase of the number of $A'$ atoms in $M_2$ or $M_3$, respectively, and $V_{21}+V_{31}$ or $V_{31}+V_{21}$ that of the number of $A$ atoms in $M_1$ at the initial stage of reaction (6), where the atomic fractions, $z_i$'s, of $A'$ atom in $M_i$'s are $z_1=1$ and $z_2=z_3=0$, respectively. $V_{21}$, $V_{31}$ and $V_{12}+V_{32}$ or $V_{21}$, $V_{31}$ and $V_{12}+V_{32}$ are defined as the rates similar to those above in a case where $z_2=1$ and $z_1=z_3=0$ or $z_1=1$ and $z_1=z_2=0$, respectively. The unidirectional rates of transfer of $A'$ atoms from $M_1$ to $M_2$, from $M_2$ to $M_1$ and so on during reaction (6) of
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a mixture of M₁, M₂ and M₃ of z₁, z₂ and z₃, respectively, are now given by
z₁V₁₂ and z₂V₂₃ etc. respectively, provided that the isotopic difference between
the transfer rates of A and A' atoms is negligible.

The net rate of reaction (6) is now given as

\[ V \equiv dN_i/dt, \]  

where \( N_i \) is the number of molecules of \( M_i \) and \( dN_i/dt \) can be expressed
in terms of \( V_{12} \) etc. as

\[
\frac{dN_i}{dt} = \frac{1}{n_i} \left\{ (V_{21} + V_{32}) - (V_{12} + V_{31}) \right\}, \quad (9.1)
\]

\[
\frac{dN_j}{dt} = \frac{1}{n_j} \left\{ (V_{12} + V_{32}) - (V_{21} + V_{31}) \right\}, \quad (9.2)
\]

\[
\frac{dN_3}{dt} = \frac{1}{n_3} \left\{ (V_{13} + V_{23}) - (V_{31} + V_{32}) \right\}. \quad (9.3)
\]

The sign, \( n_i \), in these equations denotes the number of A and A' atoms in a
molecule, \( M_i \), irrespective of their isotopic difference.

With regard to the isotopic exchanges among \( M_i \)'s, we have

\[
\frac{n_i d(N_i z_1)}{dt} = V_{31} z_3 + V_{21} z_2 - (V_{12} + V_{13}) z_i, \quad (10.1)
\]

\[
\frac{n_j d(N_j z_2)}{dt} = V_{12} z_1 + V_{32} z_3 - (V_{21} + V_{23}) z_j, \quad (10.2)
\]

\[
\frac{n_3 d(N_3 z_3)}{dt} = V_{13} z_2 + V_{23} z_2 - (V_{31} + V_{32}) z_3. \quad (10.3)
\]

Instead of \( V_+ \) in Eq. (1) we derive from Eqs. (9) and (10) the ratios,

\[ R_1 \equiv \frac{(V_{12} + V_{13})/(V_{21} + V_{23})}{(V_{31} + V_{32})}, \quad (12. \text{a}) \]

\[ R_2 \equiv \frac{(V_{21} + V_{23})/(V_{12} + V_{13})}{(V_{31} + V_{32})}, \quad (12. \text{b}) \]

It follows by substitution of \( V_{21} + V_{31} \) from Eq. (12. a) or (12. b) into Eq. (11)
that

\[ R_1 = \frac{(V_{12} + V_{13})}{(V_{21} + V_{31})} \]

\[ = 1 + n_1 (z_1 - z_2) \left( \frac{dN_1}{dt} \right) \left\{ n_1 N_1 dz_1/dt - (z_3 - z_2) V_{31} \right\} \]  \hspace{1cm} (13. a)

or

\[ R_1 = 1 + n_1 (z_1 - z_2) \left( \frac{dN_1}{dt} \right) \left\{ n_1 N_1 dz_1/dt + (z_3 - z_2) V_{21} \right\} , \]  \hspace{1cm} (13. b)

respectively.

Similarly to the above derivation of \( R_1 \) it follows from Eqs. (9.2) and (10.2) that

\[ R_2 = \frac{(V_{21} + V_{23})}{(V_{12} + V_{22})} \]

\[ = 1 - n_2 (z_1 - z_2) \left( \frac{dN_2}{dt} \right) \left\{ n_2 N_2 dz_2/dt + (z_1 - z_3) V_{32} \right\} \]  \hspace{1cm} (14. a)

or

\[ R_2 = 1 + n_2 (z_2 - z_3) \left( \frac{dN_2}{dt} \right) \left\{ n_2 N_2 dz_2/dt - (z_1 - z_3) V_{12} \right\} , \]  \hspace{1cm} (14. b)

§ 4 Analysis of the experimental results of K.O. according to Eqs. (13) and (14).

We see that the terms in the right-hand side of Eq. (13. a), (13. b), (14. a) or (14. b) are reduced to

\[ 1 + (z_1 - z_2) \frac{d}{dz_1} \ln N_1 = R_{1a}, \]  \hspace{1cm} (15. 1a)

\[ 1 + (z_1 - z_3) \frac{d}{dz_1} \ln N_1 = R_{1b}, \]  \hspace{1cm} (15. 1b)

\[ 1 - (z_1 - z_2) \frac{d}{dz_2} \ln N_2 = R_{2a}, \]  \hspace{1cm} (15. 2a)

or

\[ 1 + (z_2 - z_3) \frac{d}{dz_2} \ln N_2 = R_{2b}, \]  \hspace{1cm} (15. 2b)

in the particular case where

\[ (z_3 - z_2) V_{31} = 0, \]  \hspace{1cm} (16. a)

\[ (z_2 - z_2) V_{21} = 0, \]  \hspace{1cm} (16. b)

\[ (z_1 - z_2) V_{22} = 0, \]  \hspace{1cm} (16. 2a)

or

\[ (z_1 - z_3) V_{12} = 0, \]  \hspace{1cm} (16. 2b)

respectively. Denoting \( O_2 \), \( SO_2 \) and \( SO_3 \) by \( M_1 \), \( M_2 \) and \( M_3 \), respectively, we find that \( R_{1b} \) and \( R_{2b} \) are just the same as the terms on the right-hand side of Eqs. (4. R) and (5. R), respectively, which have been derived for \( V_+ / V_- \) by K.O.
We now investigate the magnitudes of $R_{ia}$ etc. by comparing them with $R_i$ and $R_3$ under the experimental conditions of K.O. With reference to the results of Table 1 we see that

$$z_1 \gg z_3 > z_2$$

(17)

and

$$dN_i/dt, \ dN_j/dt < 0 \ \text{and} \ dN_k/dt > 0$$

(18)
throughout the course of reaction (2). With reference to these conditions and that $V_{12}$ etc. are all positive according to their definitions, we see from Eqs. (13. a), (13. b), (15. 1a) and (15. 1b) that

$$R_{1a} \leq (V_{12} + V_{13})/(V_{21} + V_{23}) \leq R_{1a}.$$  

(19. 1)

It follows similarly from Eqs. (14. a), (14. b), (15. 2a) and (15. 2b) that

$$R_{2b} \leq (V_{21} + V_{23})/(V_{12} + V_{23}) \leq R_{2a}.$$  

(19. 2)

Table 2 shows the values of $R_{ia}$ etc. evaluated according to Eqs. (15) from the experimental results at 395°C of Table 1.

**Table 2.** The values of $R_{ia}$, $R_{1b}$, $R_{2a}$ and $R_{2b}$ at 395°C evaluated according to Eqs. (15. 1a), (15. 1b), (15. 2a) and (15. 2b), respectively, with reference to the experimental results of Table 1.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>$R_{ia}$</th>
<th>$R_{1b}$</th>
<th>$R_{2a}$</th>
<th>$R_{2b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>217.5</td>
<td>205.1</td>
<td>10.1</td>
<td>1.48</td>
</tr>
<tr>
<td>33</td>
<td>208.7</td>
<td>185.5</td>
<td>17.3</td>
<td>2.80</td>
</tr>
<tr>
<td>78</td>
<td>205.0</td>
<td>179.5</td>
<td>30.5</td>
<td>4.67</td>
</tr>
<tr>
<td>170</td>
<td>202.6</td>
<td>174.7</td>
<td>50.2</td>
<td>8.91</td>
</tr>
</tbody>
</table>

We see from Eqs. (19) and the results of Table 2 that $R_1 = (V_{12} + V_{13})/(V_{21} + V_{23})$ is ca. 200 practically independent of the progress of the reaction (2), whereas $R_2 = (V_{21} + V_{23})/(V_{12} + V_{23})$ is larger than unity, much smaller than $R_i$ and increases with the progress of the reaction. It follows from Eqs. (8), (9. 1) and (9. 2), where $m_1 = 1$, $m_2 = m_3 = 2$, $n_1 = n_2 = 2$ and $n_3 = 3$ in this case, that

$$2\left\{(V_{21} + V_{23}) - (V_{12} + V_{13})\right\} = (V_{12} + V_{23}) - (V_{21} + V_{23}),$$

which can be reduced to

$$\left\{(V_{21} + V_{23}) - (V_{12} + V_{23})\right\}/(V_{12} + V_{13}) \cong 2$$
by neglection of \((V_{21} + V_{31})\) as compared with \((V_{12} + V_{13})\) on account of the value of \(R_i\) much larger than unity. We, thus, have
\[
\frac{(V_{21} + V_{31})}{(V_{12} + V_{13})} = 2\alpha,
\]
where \(\alpha > 1\).
It follows from this equation and the definitions of \(R_i\) and \(R_2\) that
\[
\frac{(V_{12} + V_{21})}{(V_{12} + V_{13})} = 2\alpha/R_2 \tag{20.1}
\]
and
\[
\frac{(V_{21} + V_{31})}{(V_{12} + V_{31})} = 2\alpha R_1 > 1. \tag{20.2}
\]
From Eq. (20.2) we see that
\[
V_{23} \gg V_{21}, V_{21} \tag{21. a}
\]
and from Eq. (20.1) that
\[
V_{32} \geq V_{13} \tag{21. b}
\]
or
\[
V_{13} > V_{32}, V_{12} \tag{21. c}
\]
at the early or the later stage of reaction (2), where \(2\alpha/R_2 \geq 1\) or \(2\alpha/R_2 < 1\), respectively, as seen from the results of Table 2. It is concluded, with reference to the relative magnitudes of \(V_{12}\) etc. derived above, that the oxygen exchange between \(S_02\) and \(S_03\) through the direct path, \(M_2-M_3\), is much faster than those between \(O_2\) and \(S_02\) through \(M_2-M_2\) and between \(O_2\) and \(S_03\) by \(M_2-M_3\), hence that these three paths, \(M_2-M_2\) etc., do not include in common the rate-determining step of reaction (2); otherwise the rates of the exchanges through these three paths would not be different from each other.

\section{Effectiveness of the sequence of steps, (3).}

We see, with regard to the sequence of steps, (3), that the direct path, \(M_1-M_3\) or \(M_2-M_3\), consists of steps \(a\) and \(c\) or \(b\) and \(c\), respectively, hence that the conclusion of K.O. that step \(c\) common to these two paths is rate-determining for reaction (2), conflicts with the present one derived in the foregoing section.

In the foregoing section it has been shown that \(V_+/V_-\) evaluated by the treatment of K.O. is identical with \(R_{1b}\) or \(R_{2b}\) which is the lower bound of \(R_1\) or \(R_2\) respectively and obtained in the case where Eq. (16.1b) or Eq. (16.2b) is valid. It must be \(V_{12} = V_{21} = 0\) in this case on account of \(z_1 \equiv z_2 \equiv z_3\) in the experiments of K.O., that is, the direct oxygen exchange between
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$O_2$ and $SO_2$ is absent, hence it follows that

$$R_{1b} = \frac{V_{1b}}{V_{31}} \quad \text{and} \quad R_{2b} = \frac{V_{2b}}{V_{32}} \quad (22)$$

for the sequence of steps, (3).

$R_{1b}$ of Eq. (22) is the ratio of the forward unidirectional rate to that of the reverse of the oxygen transfer through the direct path, $M_1-M_3$, consisting of steps $a$ and $c$ of sequence (3) and expressed as\(^5,7\)

$$R_{1b} = \frac{v_a/v_{a-}}{v_{c+}/v_c}, \quad (23.1)$$

where $v_a$ or $v_c$ is the forward unidirectional rate of step $a$ or $c$ respectively and $v_{a-}$ or $v_{c+}$ is that of the reverse. $R_{2b}$ is similarly given as

$$R_{2b} = \frac{v_b/v_{b-}}{v_{c+}/v_c}, \quad (23.2)$$

The ratio, $v_{a-}/v_{a+}$, of step $s$ ($=a, b$ or $c$) is now recast in the form of\(^3,4\)

$$v_{a-}/v_{a+} = \exp(-\Delta G_s/RT), \quad (s=a, b \text{ or } c) \quad (24)$$

where $-\Delta G_s$ is the affinity of step $s$.

It follows from Eqs. (23), (24) and the values of $R_{1b}$ and $R_{2b}$ given in Table 2, that

$$\Delta G_a/\Delta G_b = \ln (R_{1b}/R_{2b}) = 5.1 \sim 3.0, \quad (25)$$

which vary with the progress of reaction (2). We have further by substitution of $V_{a-}/V_{a+}$ of Eq. (1) by $R_{1b}$ of Eq. (23.1) that

$$\nu(r) = -\Delta G/RT \ln R_{1b},$$

which can be recast in the form of

$$\nu(r) = \Delta G/\Delta G_a + \Delta G_c = \left(\frac{\Delta G_a}{\Delta G_b} + 2 + \frac{\Delta G_c}{\Delta G_b}\right) \left(\frac{\Delta G_a}{\Delta G_b} + \frac{\Delta G_c}{\Delta G_b}\right), \quad (26.\nu)$$

by taking Eq. (24) and

$$\Delta G = \sum_s \nu_s \Delta G_s \quad (s=a, b \text{ and } c) \quad (26.G)$$

into account, where $\nu_s$ is the stoichiometric number of step $s$ and 1, 2 or 2 for step $a$, $b$ or $c$, respectively. The value of $\nu(r)$ has been given by K.O. as $2 \sim 2.5$ and we see accordingly from Eqs. (25) and (26.\nu) that

$$\Delta G_a/\Delta G_b \simeq 0. \quad (27)$$

The values of $\nu(r)$ given in Table 1 are easily seen equal to $-\Delta G/RT \ln R_{2b}$, which is now recast in the form of

$$\nu(r) = \Delta G/\Delta G_b + \Delta G_c = \left(\frac{\Delta G_a}{\Delta G_b} + 2 + \frac{\Delta G_c}{\Delta G_b}\right) \left(1 + \frac{\Delta G_c}{\Delta G_b}\right), \quad (28)$$
similarly to the above derivation of \( \nu (r) \). Introducing the values of Eqs. (25) and (27) into above equation, we have

\[
\nu (r) = 7.1 \sim 5.0,
\]

which is qualitatively in conformity with the result of Table 1, which shows that this value is considerably larger than that evaluated by K.O. according to \( \nu (r) = -\Delta G / RT \ln R_{1b} \).

The relative magnitudes of \( \Delta G \) etc. given by Eqs. (25) and (27) are consistent, as shown in the followings, with the results of the exchange of radioactive sulfur between \( \text{SO}_2 \) and \( \text{SO}_3 \) observed by K.O. in the course of reaction (2).

Provided that this exchange is exclusively caused by sequence (3), we see that only a part of oxygen exchange between \( \text{SO}_2 \) and \( \text{SO}_3 \) through the direct path, \( \text{M}_2 \text{M}_3 \), results in the sulfur exchange between them, as exemplified by the following exchanges.

\[
\text{S}^* \text{OO}' + \text{SO}_3 \leftarrow \text{S}^* \text{O}_2 + \text{SO}_3 \text{O}'
\]

\[
\leftarrow \text{S}^* \text{O}_2 \text{O}' + \text{SO}_2
\]

where \( \text{S}^* \) denotes an atom of the radioactive sulfur. The second one of the above oxygen exchanges simultaneously results in that of sulfur, but not the first one. Provided that a common fraction, \( \beta \), of \( V_{23} \) and \( V_{32} \) contributes to the sulfur exchange between \( \text{SO}_2 \) and \( \text{SO}_3 \), we have from Eqs. (9.2) and (10.2) with regard to this exchange that

\[
n_2 dN_2 / dt = V_{32} - V_{23}
\]

and

\[
n_2 d(N_2 z'_2) / dt = \beta z'_2 V_{32} - \beta z'_2 V_{23},
\]

by taking \( V_{12} = V_{21} = 0 \) into account, where \( z'_2 \) or \( z'_3 \) is the mole fraction of radioactive \( \text{SO}_2 \) or \( \text{SO}_3 \) respectively. It follows from these equations that

\[
V_{23} / V_{32} = 1 + n_2 (dN_2 / dt) (z'_2 - \beta z'_2) \left[ n_2 N_2 d z'_2 / dt - (1 - \beta) z'_2 V_{23} \right]. \tag{29}
\]

In the treatment of K.O. \( V_+ / V_- \) in Eq. (1) was replaced by \( V_{23} / V_{32} \) of Eq. (29), where \( \beta \) was \textit{a priori} treated as unity and \( \nu (r) \) was estimated at 2.0 \sim 2.5. Taking \( \beta < 1 \) and the experimental condition of K.O. that

\[
dN_2 / dt < 0, \; d z'_2 / dt < 0 \; \text{and} \; z'_2 > z'_3
\]

into account, we see that the value of \( V_+ / V_- \) evaluated by K.O. is the upper bound of \( V_{23} / V_{32} \) of Eq. (29). The value of \( \nu (r) \) of K.O. is accordingly the lower bound of that correctly evaluated according to Eq. (29) and
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\[ \nu(r) = -\frac{\Delta G}{RT} \ln \left( \frac{V_2}{V_3} \right). \] (30)

\( \nu(r) \) of Eq. (30) is now given by Eq. (28) and evaluated with reference to Eqs. (25) and (27) as 7.1~5.0 in conformity with the above estimation.

Summarizing the above discussions, we see that the sequence of steps, (3), assumed by K.O., is effective in a consistent interpretation of their experimental results, however, it results in a conclusion that the step, \( \text{SO}_2(a) + O(a) \rightleftharpoons \text{SO}_3 \), is nearly in equilibrium and the step, \( O_2 \rightleftharpoons 2O(a) \), slower than the step, \( \text{SO}_2 \rightleftharpoons \text{SO}_2(a) \), according to the results of the present analysis that \( \Delta G_c/\Delta G_b \approx 0 \) and \( \Delta G_a/\Delta G_b = 5.1 \sim 3.0 \).

The present result that the value of \( \Delta G_a/\Delta G_b \) varies from 5.1 to 3.0 with the progress of the oxidation of \( \text{SO}_2 \), is difficult to understand for the present. This variation may be caused by the experimental error of K.O., who have not observed the concentration of \( \text{SO}_2 \) and the atomic fraction of heavy oxygen in \( \text{SO}_2 \), but estimated them according to the assumed mass balances of sulfur and respective isotopes of oxygen, or may show the necessity of some improvement of the sequence of steps assumed by K.O. A further detailed discussion of this point is, however, not given for the present.

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Appendix

Discriminating between normal and heavy oxygen atoms, \( O \) and \( O' \) respectively, the sequence of steps, (7), in the text is developed into the following eleven steps.
M. Masuda and K. Miyahara

\[ s = 1 : \quad O_2 \rightleftharpoons 2O(a), \]
\[ 2 : \quad OO' \rightleftharpoons O(a) + O'(a), \]
\[ 3 : \quad SO_2 \rightleftharpoons SO_2(a), \]
\[ 4 : \quad SOO' \rightleftharpoons SOO'(a), \]
\[ 5 : \quad SO_2(a) + O(a) \rightleftharpoons SO_2(a), \]
\[ 6 : \quad SO_2(a) + O'(a) \rightleftharpoons SO_2O'(a), \]
\[ 7 : \quad SOO'(a) + O(a) \rightleftharpoons SO_2O'(a), \]
\[ 8 : \quad SOO'(a) + O'(a) \rightleftharpoons SO_2O'(a), \]
\[ 9 : \quad SO_3(a) \rightleftharpoons SO_3, \]
\[ 10 : \quad SO_2O'(a) \rightleftharpoons SO_2O', \]
\[ 11 : \quad SOO'(a) \rightleftharpoons SOO', \]

(A.1)

where \( O', SO'_2 \) and \( SO'_3 \) are neglected to simplify the argument by assuming that the concentration of \( O' \) atoms in the reaction system is low enough.

The steady state condition of a reaction consisting of \( I' \) intermediates and \( S \) steps is given as \(^{4,8}\),

\[
(a_i)\{v_s\} = 0, \quad (i = 1, 2, \cdots, I', \quad s = 1, 2, \cdots, S)
\]

(A.2)

where \( a_{is} \) is an element of \( i \)-th row and \( s \)-th column of matrix \( (a_{is}) \) and denotes the number of \( i \)-th intermediate formed by a forward act of step \( s \) and \( \{v_s\} \) a column matrix of the net rate, \( v_s \), of step \( s \). \( (a_{is}) \) is now given with regard to the set of steps, \( (A.1) \), as

\[
(a_{is}) = \begin{pmatrix}
2 & 1 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 & 0
\end{pmatrix}
\]

(A.3)

The number, \( P \), of the particular solution of Eq. (A.2) is that of routes of reaction linearly independent with each other\(^{4,4}\), and given by \( P = S - I \), where \( I \) is the rank of matrix \( (a_{is}) \) and seven in this case, hence \( P = 11 - 7 = 4 \). The four linearly independent routes of reaction are given as

\[
\{v_s\}_1 = C_1 \{ 1, -1, -1, 1, 0, -1, 1, 0, 0, 0, 0 \},
\]

\[
\{v_s\}_2 = C_2 \{ 1, 0, 2, 0, 2, 0, 0, 0, 2, 0, 0 \},
\]

(A.4)
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\[
\begin{align*}
\{v_1\}_3 &= C_3 \{-1, 2, 2, 0, 0, 2, 0, 0, 2, 0\}, \\
\{v_2\}_4 &= C_4 \{-3, 2, 0, 0, 2, -2, 0, 0, 2, 0\},
\end{align*}
\]

where \(C_1\) etc. are arbitrary constants equal to the steady rates of the overall reactions caused by these routes respectively. The four routes linearly independent with each other are not necessarily those of (A.4) themselves, but also their linear combinations.

The second route of (A.4) results in the steady oxidation of sulfur dioxide, i.e.,

\[2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3. \quad \text{(A.5.1)}\]

The first one of (A.4) results in

\[\text{O}_2 + \text{SO}_2\text{O} = \text{OO}'+\text{SO}_2. \quad \text{(A.5.2)}\]

By the linear combinations of routes of (A.4) that

\[
\{v_1\}_3 + \{v_2\}_4 \quad \text{with} \quad C_3 = -C_4 = \frac{1}{2},
\]

\[
\{v_1\}_4 + \{v_2\}_3 + \{v_3\}_4 \quad \text{with} \quad C_1 = 1, \quad -C_3 = C_4 = \frac{1}{2},
\]

and

\[
\{v_1\}_4 + \{v_2\}_3 + \{v_3\}_2 + \{v_4\}_4 \quad \text{with} \quad C_1 = C_3 = 1, \quad C_2 = C_4 = -\frac{1}{2},
\]
it follows as the overall reactions that

\[
\begin{align*}
\text{O}_2 + \text{SO}_2\text{O} &= \text{OO}'+\text{SO}_2\text{O}', \\
\text{SO}_2\text{O} + \text{SO}_2\text{O}' &= \text{SO}_2 + \text{SO}_3.
\end{align*}
\]

and

\[
\text{SO}_2 + \text{SO}_2\text{O}' = 2\text{SO}_3\text{O}'. \quad \text{(A.5.5)}
\]

respectively. (A.5.2), (A.5.3) and (A.5.4) are the oxygen exchanges between \(\text{O}_2\) and \(\text{SO}_2\), between \(\text{O}_2\) and \(\text{SO}_3\) and between \(\text{SO}_2\) and \(\text{SO}_3\), respectively, and (A.5.5) the equilibration of oxygen isotopes among \(\text{SO}_3\). Four from these five overall reactions, (A.5.1) etc., are linearly independent with each other as mentioned above.

In a case where \(\text{O}_2', \text{SO}_2'\) and \(\text{SO}_3'\) are taken into account, \(S\) and \(I\) are 16 and 9 respectively, hence we have seven routes of reaction linearly independent with each other, to which we can apply the equilibration of oxygen isotopes among gaseous oxygen molecules, i.e.

\[\text{O}_2 + \text{O}_2' = 2\text{OO}',\]

and that among sulfur dioxide molecules, i.e.
SO₂ + SO₃' = 2SOO',
as well as the five reactions given above. These three equilibrations are not necessary for the present analysis, as it concerns with the atomic fractions of heavy oxygen in oxygen, sulfur dioxide and sulfur trioxide, but not with its detailed distributions among them. We, thus, see that oxygen exchanges between any two of oxygen, sulfur dioxide and sulfur trioxide caused by the sequence of steps, (7), are direct, that is, linearly independent with each other.