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# ON THE MECHANISM OF THE OXIDATION OF SULFUR DIOXIDE

## Part II: Determination of the Stoichiometric Number of Rate-Determining Step by Means of $^{18}O$

By

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### Abstract

Stoichiometric number $\nu(r)$ of the rate-determining step of catalyzed oxidation of $SO_2$,

$$2SO_2 + O_2 = 2SO_3,$$

in the presence of Pt catalyst was determined to be 2 at 395° and 405°C by following the unidirectional reaction rate by means of $^{18}O$ as tracer.

Incorporating the present result with the previous one[1] that $\nu(r)$ is found 2 by means of $^{35}S$, it is concluded that the last step of the sequence, $O_2 \rightarrow 2O(a)$, $SO_2 \rightarrow SO_2(a)$ and $O(a) + SO_2(a) \rightarrow SO_3$, of the above overall reaction is rate-determining, where (a) signifies the adsorbed state.

## I. Introduction

The present paper is devoted to estabish the mechanism of the catalyzed oxidation of sulfur dioxide,

$$2SO_2 + O_2 = 2SO_3 \tag{1}$$

in the presence of platinum catalyst by determining the stoichiometric number $\nu(r)$ of the rate-determining step by means of oxygen isotope in conjunction with the previous result obtained by means of sulfur isotope.

Reaction (1) is assumed to proceed through the sequence of steps shown in the first column in Table 1, the stoichiometric number $\nu$'s of respective steps being given in the next column headed by $\nu$. According to the theory of steady reaction, the stoichiometric number $\nu(r)$ of rate-determining step is expressed[2] as

$$\nu(r) = -\Delta G/RT \ln(V_+/V_-), \tag{2}$$

where $V_+$ or $V_-$ is the forward or backward unidirectional rate of overall

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TABLE 1. Stoichiometric number $\nu$ and its value $\nu(\mathrm{r})$ of rate-determining step as determined with isotope.

| Constituent step*) | Stoichiometric number | | |
|---|---|---|---|
| | $\nu$ | $\nu(\mathrm{r})$ | |
| | | $^{35}S$ | $^{18}O$ |
| $O_2 \longrightarrow 2O(a)$ | 1 | $\infty$ | 1 |
| $SO_2 \longrightarrow SO_2(a)$ | 2 | 2 | $\infty$ |
| $SO_2(a)+O(a) \longrightarrow SO_3$ | 2 | 2 | 2 |

*) (a) signifies the adsorbed state.

reaction at the steady state, $-\Delta G$ the affinity of overall reaction and other notations are of usual meaning.

The $V_+$ or $V_-$ is determined as below by means of an appropriate isotope as tracer. The rate of transfer of isotope, *e.g.* $^{18}O$ from oxygen to sulfur trioxide in course of reaction (1) is given as

$$-d(n^{O_2}Z^{O_2})/dt = Z^{O_2}V_+ - Z^{SO_3}V_- , \qquad (3)$$

provided that the transfer is effected solely through the completion of overall reaction (1), where $Z^{O_2}$ or $Z^{SO_3}$ is the atomic fraction of $^{18}O$ in $O_2$ or $SO_3$ respectively, and $n^{O_2}$ is the number of moles of oxygen in the reaction system. The completion of reaction (1) is necessary for the transfer of $^{18}O$ from $O_2$ to $SO_3$, if, *e.g.* the last step be rate-determining. If, on the other hand, the second step be rate-determining, $^{18}O$ in $O_2$ is transferred to $SO_3$ by the first and third steps without the rate-detemining second step, hence without the completion of reaction (1). Eq. (3) determines $V_+$ and $V_-$ in term of observable quantities, when solved simultaneously with the equation

$$-dn^{O_2}/dt = V_+ - V_- \qquad (4)$$

of the directly measurable net rate $-dn^{O_2}/dt$ of rection (1). In terms of $V_+$ and $V_-$ thus determined, (2) yields apparently extravagantly large value of $\nu(r)$, in case where transfer of isotope occurs without the completion of the overall reaction as has been shown by MATSUDA and HORIUTI[3]. Denoting such a value of $\nu(r)$ conventionally by $\infty$, we have $\nu(r)$-value shown in Table 1 for the rate-determining step indicated in the appropriate row and for the kind of tracer entered at the head of the appropriate column.

The $\nu(r)$ of reaction (1) has now been determined in Part 1[1] to be 2 by means of $^{35}S$ as tracer. It follows with reference to Table 1 that the rate-determining step is either the second or the last one but not the first one and that the rate-determining step is finally decided by a similar determination of $\nu(r)$ by means of oxygen isotope.

The requisite determination of $\nu(r)$ has been carried out in the present work at 395° and 405°C. For the practical determination of $\nu(r)$ (2) is developed as follows. The $\Delta G$ in (2) is expressed in terms of partial pressures $P^{SO_2}$, $P^{SO_3}$ and $P^{O_2}$ of sulfur dioxide etc. and equilibrium constant $K$ as[4)]

$$-\Delta G = RT\ln\left\{(P^{SO_2})^2\cdot P^{O_2}\cdot K/(P^{SO_3})^2\right\}. \qquad (5)$$

We have, on the other hand, (3) for the tracer of $^{18}O$ ignoring isotope effect. Eliminating $V_+$, $V_-$ and $\Delta G$ from (2), (3), (4) and (5), we have

$$\nu(r) = \frac{\log[(P^{SO_2})^2 P^{O_2} K/(P^{SO_3})^2]}{\log[1-(Z^{SO_3}-Z^{O_2})\,d\ln P^{O_2}/dZ^{O_2}]} \qquad (6)$$

which allows us to determine $\nu(r)$-value in Table 1 in every stage of reaction from directly observable quantities on the right-hand side of (6).

## II. Materials

Sulfur dioxide; Research grade sulfur dioxide supplied by the SYOWA DENKO Ltd., Tokyo was washed with conc. sulfuric acid, condensed with liquid nitrogen and noncondensable gas evacuated. The condensate was now distilled three times from −80°C to liquid nitrogen temperature in order to remove the last trace of water, which upset the expeiment by forming sulfuric acid with sulfur trioxide as mentioned in Part I. Final sample thus purified was about one nineth of the original in volume.

Heavy oxyen; Water containing $^{18}O$ supplied by the RESEARCH AND DEVELOPEMENT Ltd., Rehovoth, Israel was electrolyzed by platinum electrodes and the gas evolved at the anode was purified through a column of platinum asbestos kept at about 300°C and two liquid nitrogen traps.

Platinum catalyst; 10.2 gm platinum gauze of 0.1 mm diameter wire drawn from TOKURIKI Ltd., Tokyo was electrolytically platinized freshly for every of experiment.

## III. Apparatus

The apparatus used for the reaction is the same as that in part I, except that the whole apparatus was made of pyrex and flask $V_1$ of one litter capactiy containing heavy oxygen was incorporated beforehand into the apparatus as shown in Fig. 1.

Fig. 2 shows the apparatus for separation of sulfur dioxide and oxygen

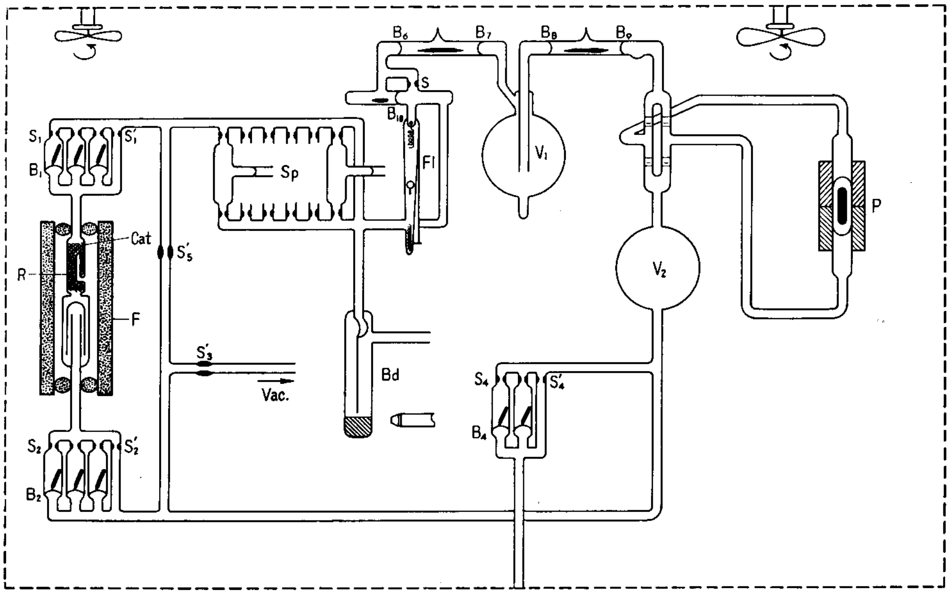

**Fig. 1.** Apparatus for following reaction $2SO_2+O_2=2SO_3$.

R : Reactor
Fl : Flow meter
Cat : Catalyst
Sp : Sampling tubes
Bd : Bourdon's gauge
$V_1$, $V_2$ : Flasks
F : Electric furnace
P : Circulating pump
$B_1 \cdots B_{10}$ : Breakable joints
S : Orifice
$S_5 \cdots S_1$, $S_1' \cdots S_5'$ : Constrictions

from sulfur dioxide in the sampled gas. Sp is a sampling tube, T liquid nitrogen trap, M a receiver of 500 ml volume of separated sulfur dioxide and oxygen. RMS-3B type mass spectrometer from HITACHI Ltd., Tokyo was used for the analysis of atomic fractions of $^{18}O$ in oxygen and sulfur dioxide.

## IV. Experimental Procedure

Reaction (1) was followed at 395° and 405°C with oxygen labelled with $^{18}O$ by measuring the total pressure and the atomic fractions of $^{18}O$ in $SO_2$ and $O_2$, sampling the gas mixture time to time in course of the progress of reaction.

The experimental procedure of following reaction (1) was, as described below, the same as in Part 1[1] except for a few points. Keeping the reactor at 405°C and remaining part A of the apparatus at 80°C, the whole apparatus, except reservoir $V_1$ of heavy oxygen, was evacuated through constrictions $S_3'$ and $S_4'$ to $10^{-5}$ mmHg. Constrictions $S_1'$, $S_2'$, $S_3'$, $S_4'$ were now sealed to shut off A from the vacuum line and to isolate the reactor from A. Heavy oxygen

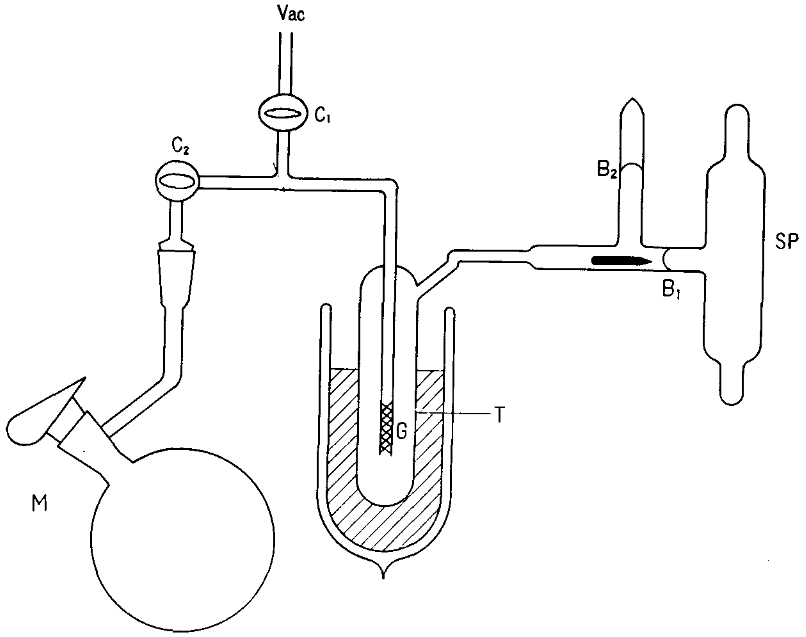

**Fig. 2.** Apparatus for separation of $SO_2$ and $O_2$ from sampled gas.

| | |
|---|---|
| Sp: Sampling tube | T: Trap |
| M: Flask | G: Glass wool |
| $B_1$, $B_2$: Breakable joints | |

in $V_1$ was now allowed to expand into A through orifice S by opening breakable joints, $B_7$ and $B_6$, the resulting pressure $P_A^{O_2}$ being determined as that outside the BOURDON's gauge adjusted to compensate that inside.

As the pressure in A thus attained a constant value, $B_8$, $B_9$ and $B_{10}$ were opened. Opening then one of breakable joints $B_4$'s, sulfur dioxide was admitted into A twice as much as heavy oxygen, and the constriction $S_4$ communicated with the opened $B_4$ was sealed off. The gases thus admitted were mixed by circulating them for an hour by means of *P*. The partial pressure $P_A^{SO_2}$ of $SO_2$ in A is thus $P_A^{SO_2} = 2P_A^{O_2}$. The reactor was now kept at the desired temperature of reaction, $S_5'$ was sealed and one of $B_2$'s as well as one of $B_1$'s was opened to circulate gas mixture through the reactor. The reactor was kept at a constant temperature within 0.5°C few minutes after the beginning of the circulation which was usually followed by a drop of temperature by ca. 1°C. The constant temperature was elevated or lowered, in case where the reaction rate roughly observed by the BOURDON gauge was too slow or too rapid respectively in order to secure an expedient observation. As the temperature settled down to an appropriate constant value at a constant rate of circulation, the circulating gas was sampled into one of Sp's by sealing off the constrictions at its both ends. The reaction was allowed to proceed furthur at the same condition and the circulating gas was sampled another five times after each decrease of the total pressure by approximately constant an amount.

Initial partial pressure $P_0^{O_2}$ of oxygen was calculated from its partial pressure $P_A^{O_2}$ in A by an equation

$$P_A^{O_2} V_A / T_A = P_0^{O_2} ( V_R / T_R + V_A / T_A ) ,$$

where $V_A$ or $V_R$ is the volume of $A$ or $R$ respectively determined preliminarily and $T_A$ or $T_R$ the absolute tempeature of $A$ or $R$ respectively. The initial partial pressure $P_0^{SO_2}$ of $SO_2$ is twice as large as $P_0^{O_2}$ according to the above experimental procedure.

We have from the stoichiometry of reaction (1)

$$2 ( P_0^{O_2} - P^{O_2} ) = P^{SO_3} .$$

Noting that

$$P = P^{O_2} + P^{SO_2} + P^{SO_3}$$

and

$$2 P^{O_2} = P^{SO_2} ,$$

we have

$$P^{O_2} = P - 2 P_0^{O_2} , \qquad P^{SO_2} = 2 P - 4 P_0^{O_2}$$

and

$$P^{SO_3} = 2 ( 3 P_0^{O_2} - P ) .$$

$SO_2$ and $O_2$ in a sample were separated from $SO_3$ as follows by fusing trap T to the sampling tube Sp as shown in Fig. 2. After the space outside $B_1$ was evacuated to $10^{-5}$ mmHg tap $C_1$ was closed, T immersed in liquid nitrogen and breakable joint $B_1$ opened to transfer $O_2$, $SO_2$ and $SO_3$ in the sampling tube into T. Bath of T was now changed to that of alcohol at −8°C and noncondensing gases, *i.e.* $O_2$ and $SO_2$, in T were allowed to expand into flask M by opening tap $C_2$. M was now attached to mass spectrometer and its contents were anlyzed for the atomic fraction $Z^{SO_2}$ of $^{18}O$ in $SO_2$ and that $Z^{O_2}$ in $O_2$. Atomic fraction $Z^{SO_3}$ of $^{18}O$ in sulfur trioxide was calculated from $P^{O_2}$, $P^{SO_2}$, $Z^{O_2}$, $Z^{SO_2}$ and $P^{SO_3}$ by the equation

$$Z^{SO_3} = 2 ( P_0^{O_2} Z_0^{O_2} + P_0^{SO_2} Z_0^{SO_2} - P^{O_2} Z^{O_2} - P^{SO_2} Z^{SO_2} ) / 3 P^{SO_3} ,$$

where $Z_0^{O_2}$ and $Z_0^{SO_2}$ are initial atomic fractions of $^{18}O$ in $O_2$ and $SO_2$ respectively.

## V. Result

Results of experiments at 395° and 405°C are summarized in Table 2 and 3. "Time of reaction" is the time elapsed from the first sampling up to the appropriate sampling. Fig. 3 shows total pressure $P$ *versus* time. Fig. 4 and 5 are plots of $Z^{SO_3}$ and $Z^{O_2}$ against $\log P^{O_2}$ at 395° and 405°C respectively, from which the value of $d \ln P^{O_2}/dZ^{O_2}$ in (6) is determined with the aid of prism[5]. Equilibrium constant $K$ at 395° or 405°C was determined from an empirical equation

$$\log K = 1.066 \times 10^4/T - 9.996$$

which summarizes the observation of $P^{SO_2}$, $P^{O_2}$ and $P^{SO_3}$ in equilibrium in Part

TABLE 2. Observation of Reaction $2SO_2 + O_2 = 2SO_3$ at 395°C.
$P_0^{O_2} = 19.81$ cmHg, $P_0^{SO_2} = 37.18$ cmHg, $Z_0^{O_2} = 0.1010$

| Time of reaction min | Total Pressure cmHg | $p^{SO_2}$ cmHg | $p^{SO_3}$ cmHg | $Z^{O_2}$ $\times 10^2$ | $Z^{SO_2}$ $\times 10^2$ | $Z^{SO_3}$ $\times 10^2$ |
|---|---|---|---|---|---|---|
| 0 | 50.08 | 23.34 | 13.84 | 9.96 | 1.40 | 1.87 |
| 33 | 45.74 | 14.67 | 22.50 | 9.94 | 1.73 | 2.63 |
| 55 | 44.30 | 11.80 | 25.38 | | | |
| 78 | 43.58 | 10.36 | 26.82 | 9.94 | 1.87 | 2.88 |
| 100 | 43.01 | 9.22 | 27.96 | | | |
| 135 | 43.22 | 7.64 | 29.54 | | | |
| 170 | 41.88 | 6.96 | 30.22 | 9.92 | 1.95 | 3.05 |

TABLE 3. Observation of Reaction $2SO_2 + O_2 = 2SO_3$ at 405°C
$P_0^{O_2} = 11.87$ cmHg, $P_0^{SO_2} = 24.29$ cmHg, $Z_0^{O_2} = 0.1118$

| Time of reaction hr. | Total pressure cmHg | $p^{SO_2}$ cmHg | $p^{SO_3}$ cmHg | $Z^{O_2}$ $\times 10^2$ | $Z^{SO_2}$ $\times 10^2$ | $Z^{SO_3}$ $\times 10^2$ |
|---|---|---|---|---|---|---|
| 0 | 32.45 | 16.87 | 7.42 | 11.02 | 1.64 | 2.43 |
| 0.33 | 31.89 | 15.69 | 8.62 | | | |
| 1.16 | 31.00 | 13.96 | 10.33 | 11.00 | 1.93 | 2.84 |
| 2.16 | 20.05 | 12.06 | 12.23 | | | |
| 3.75 | 28.82 | 9.59 | 14.70 | 10.97 | 2.26 | 3.35 |
| 5.16 | 27.76 | 7.48 | 16.81 | | | |
| 7.92 | 16.26 | 4.49 | 19.80 | 10.80 | 2.52 | 3.73 |
| 12.83 | 25.27 | 2.50 | 21.79 | | | |

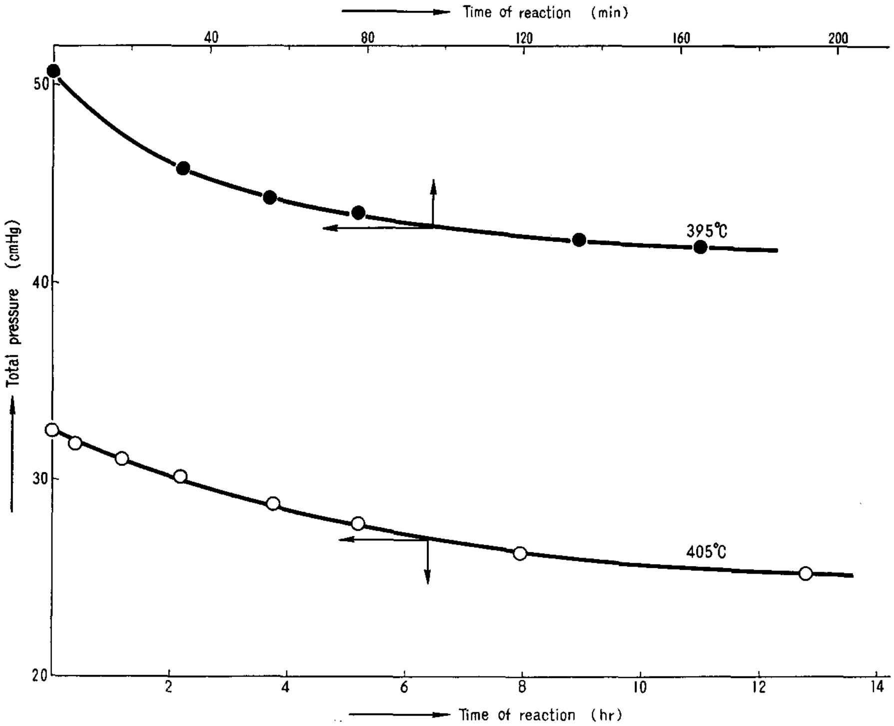

**Fig. 3.** Total pressure *vs.* time of reaction.

1. Stoichiometric number $\nu(r)$ of the rate-determining step is now determined according to (6) at several values of $-\Delta G$ substituting the values of $d \ln P^{O_2}/dZ^{O_2}$, determined as above, $Z^{SO_3}$ and $Z^{O_2}$. Fig 6 shows $\nu(r)$ thus determined plotted against the affinity $-\Delta G$.

Fig. 6 shows that the stoichiometric number $\nu(r)$ of reaction (1) is 2 but not $\infty$ as determined with $^{18}O$.

## VI. Conclusion

The stoichiometric number of the rate-determining step was 2 as determined with $^{18}O$. Incorporating the present result with the previous one[1] that $\nu(r)=2$ as determined with $^{35}S$, it is concluded with reference to Table 1 that the rate-determining step is the last one of the sequence

$$\begin{aligned} O_2 &\longrightarrow 2O(a) \\ SO_2 &\longrightarrow SO_2(a) \\ O(a)+SO_2(a) &\longrightarrow SO_3 . \end{aligned}$$

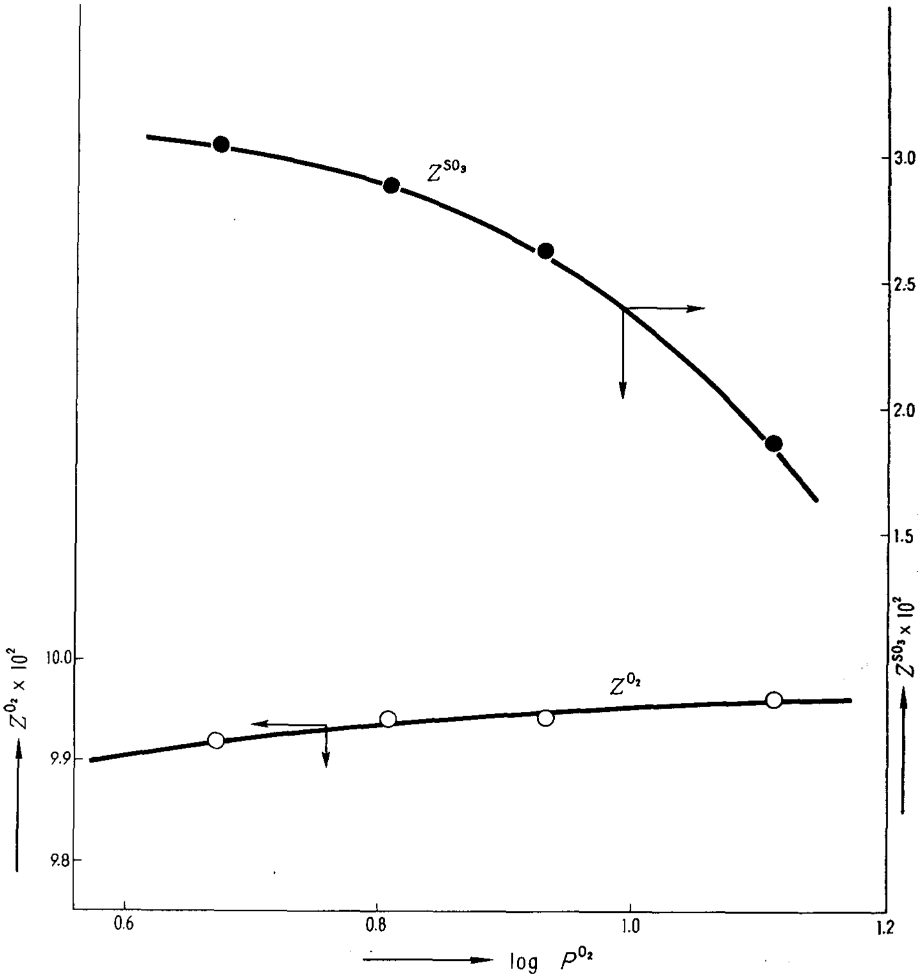

**Fig. 4.** Atomic fraction of $^{18}O$, $Z^{O_2}$ and $Z^{SO_3}$ *vs.* log $P^{O_2}$ 395°C.

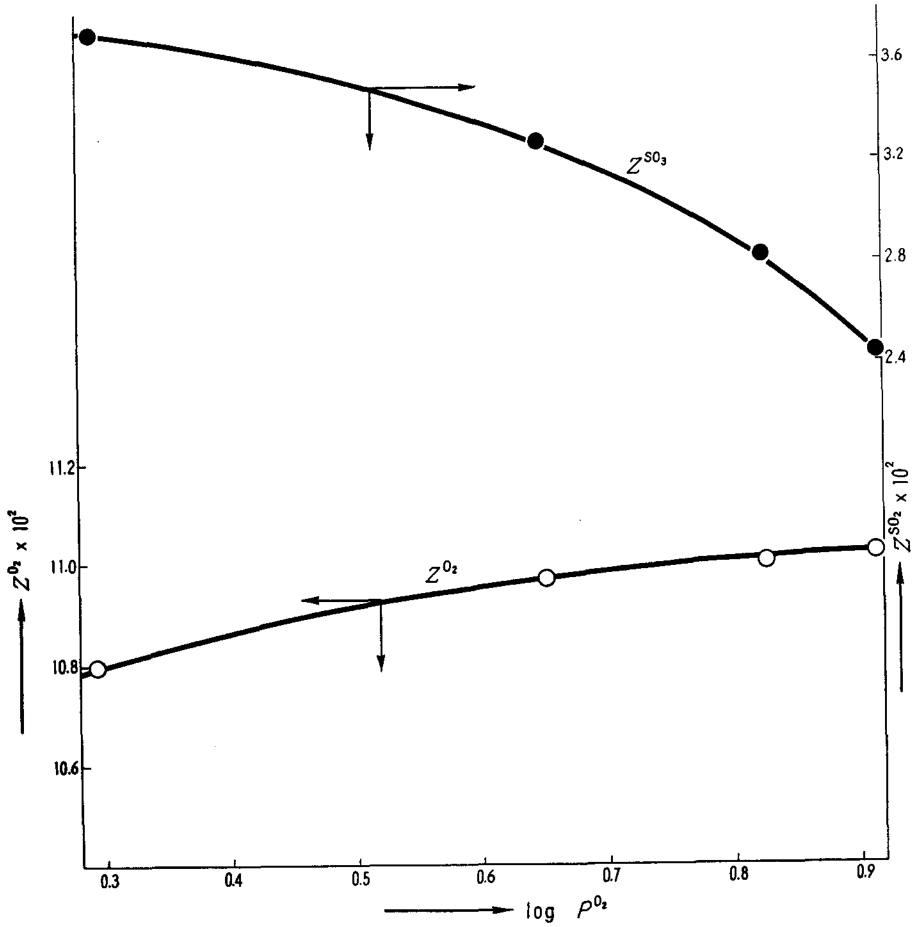

**Fig. 5.** Atomic froctions of $^{18}O$, $Z^{O_2}$ and $S^{SO_3}$ *vs.* log $P^{O_2}$, 405°C.

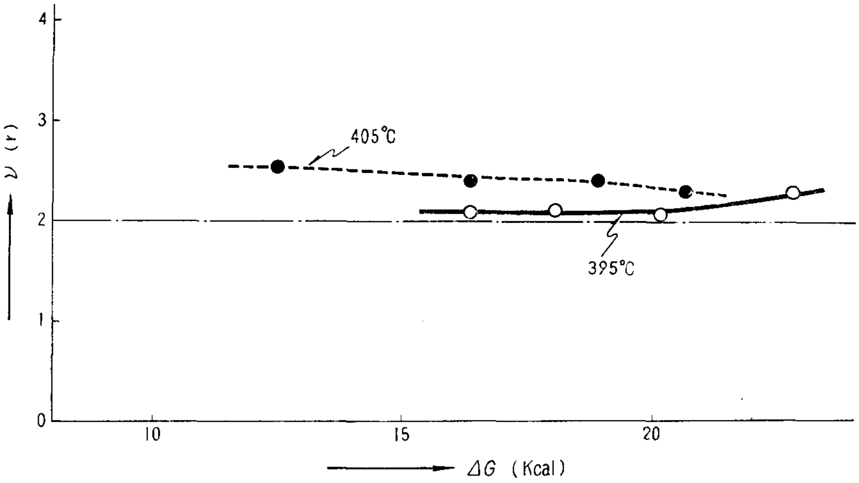

**Fig. 6.** Stoichiometric number $\nu$ (r) of rate-determining step *vs.* affinity.

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