



Title	ON THE MECHANISM OF THE OXIDATION OF SULFUR DIOXIDE : Part : Determination of the Stoichiometric Number of Rate-Determining Step by Means of ^{18}O
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 14(3), 213-223
Issue Date	1967-03
Doc URL	http://hdl.handle.net/2115/24818
Type	bulletin (article)
File Information	14(3)_P213-223.pdf



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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

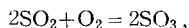
By

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(Received September 29, 1966)

Abstract

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



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 one¹⁾ that $\nu(r)$ is found 2 by means of ^{35}S , it is concluded that the last step of the sequence, $\text{O}_2 \rightarrow 2\text{O}(\text{a})$, $\text{SO}_2 \rightarrow \text{SO}_2(\text{a})$ and $\text{O}(\text{a}) + \text{SO}_2(\text{a}) \rightarrow \text{SO}_3$, of the above overall reaction is rate-determining, where (a) signifies the adsorbed state.

I. Introduction

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



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 ν 's of respective steps being given in the next column headed by ν . According to the theory of steady reaction, the stoichiometric number $\nu(r)$ of rate-determining step is expressed²⁾ as

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

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

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

Constituent step*)	Stoichiometric number		
	ν	$\nu(r)$	
		^{35}S	^{18}O
$\text{O}_2 \longrightarrow 2\text{O(a)}$	1	∞	1
$\text{SO}_2 \longrightarrow \text{SO}_2(\text{a})$	2	2	∞
$\text{SO}_2(\text{a}) + \text{O(a)} \longrightarrow \text{SO}_3$	2	2	2

*) (a) signifies the adsorbed state.

reaction at the steady state, $-dG$ 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

$$-d(n^{0_2}Z^{0_2})/dt = Z^{0_2}V_+ - Z^{SO_3}V_-, \quad (3)$$

provided that the transfer is effected solely through the completion of overall reaction (1), where Z^{0_2} or Z^{SO_3} is the atomic fraction of ^{18}O in O_2 or SO_3 respectively, and n^{0_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-determining 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

$$-dn^{0_2}/dt = V_+ - V_- \quad (4)$$

of the directly measurable net rate $-dn^{0_2}/dt$ of reaction (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 HORIUTI³⁾. Denoting such a value of $\nu(r)$ conventionally by ∞ , 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 1¹⁾ 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

On the Mechanism of the Oxidation of Sulfur Dioxide, Part II

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 ΔG in (2) is expressed in terms of partial pressures P^{SO_2} , P^{SO} , and P^{O_2} of sulfur dioxide etc. and equilibrium constant K as⁴⁾

$$-\Delta G = RT \ln \left\{ (P^{\text{SO}_2})^2 \cdot P^{\text{O}_2} \cdot K / (P^{\text{SO}})^2 \right\}. \quad (5)$$

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

$$\nu(r) = \frac{\log [(P^{\text{SO}_2})^2 P^{\text{O}_2} K / (P^{\text{SO}})^2]}{\log [1 - (Z^{\text{SO}_2} - Z^{\text{O}_2}) d \ln P^{\text{O}_2} / dZ^{\text{O}_2}]} \quad (6)$$

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 experiment by forming sulfuric acid with sulfur trioxide as mentioned in Part I. Final sample thus purified was about one ninth of the original in volume.

Heavy oxygen; 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 capacity 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

Yoshihisa KANEKO and Hideo ODANAKA

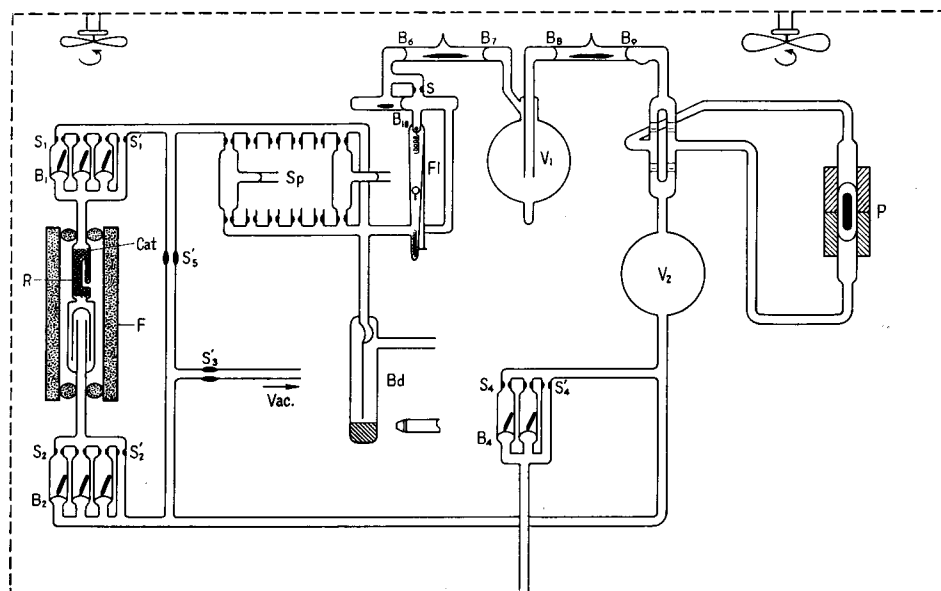


Fig. 1. Apparatus for following reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$.

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
$S_5 \cdots S_{10}, S'_1 \cdots S'_5$: 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 1¹⁾ 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

On the Mechanism of the Oxidation of Sulfur Dioxide, Part II

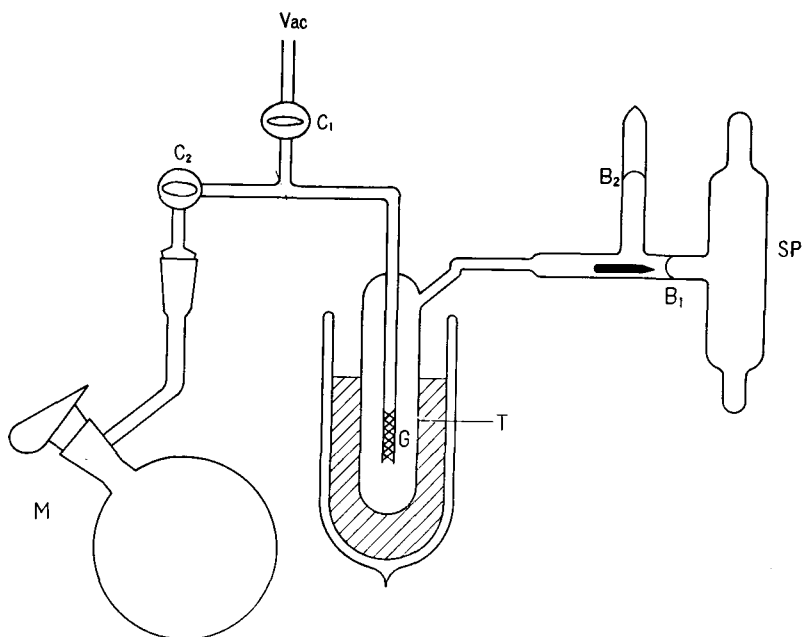


Fig. 2. Apparatus for separation of SO_2 and O_2 from sampled gas.

Sp: Sampling tube T: Trap
M: Flask G: Glass wool
B₁, B₂: 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^0 , 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 $P_A^{\text{SO}_2}$ of SO_2 in A is thus $P_A^{\text{SO}_2} = 2P_A^0$. 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 tempera-

ture 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 further 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 temperature 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)

$$2(P_0^{O_2} - P^{O_2}) = P^{SO_2}.$$

Noting that

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

and

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

we have

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

and

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

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 $-8^\circ C$ 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 analyzed 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

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

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

On the Mechanism of the Oxidation of Sulfur Dioxide, Part II

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_2} and Z^{O_2} against $\log P^{\text{O}_2}$ at 395° and 405°C respectively, from which the value of $d \ln P^{\text{O}_2} / dZ^{\text{O}_2}$ in (6) is determined with the aid of prism⁵). 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 $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ at 395°C.

$$P_0^{\text{O}_2} = 19.81 \text{ cmHg}, P_0^{\text{SO}_2} = 37.18 \text{ cmHg}, Z_0^{\text{O}_2} = 0.1010$$

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 $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ at 405°C

$$P_0^{\text{O}_2} = 11.87 \text{ cmHg}, P_0^{\text{SO}_2} = 24.29 \text{ cmHg}, Z_0^{\text{O}_2} = 0.1118$$

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			

Yoshihisa KANEKO and Hideo ODANAKA

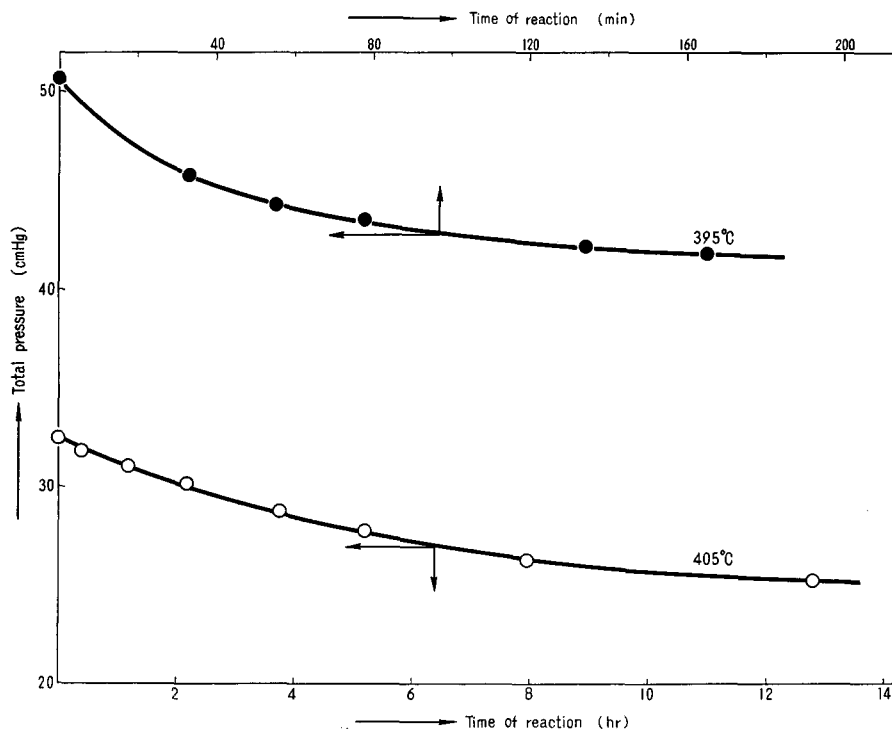


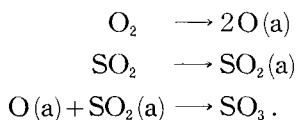
Fig. 3. Total pressure vs. time of reaction.

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_2} 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 ∞ 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 one¹⁾ 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



On the Mechanism of the Oxidation of Sulfur Dioxide, Part II

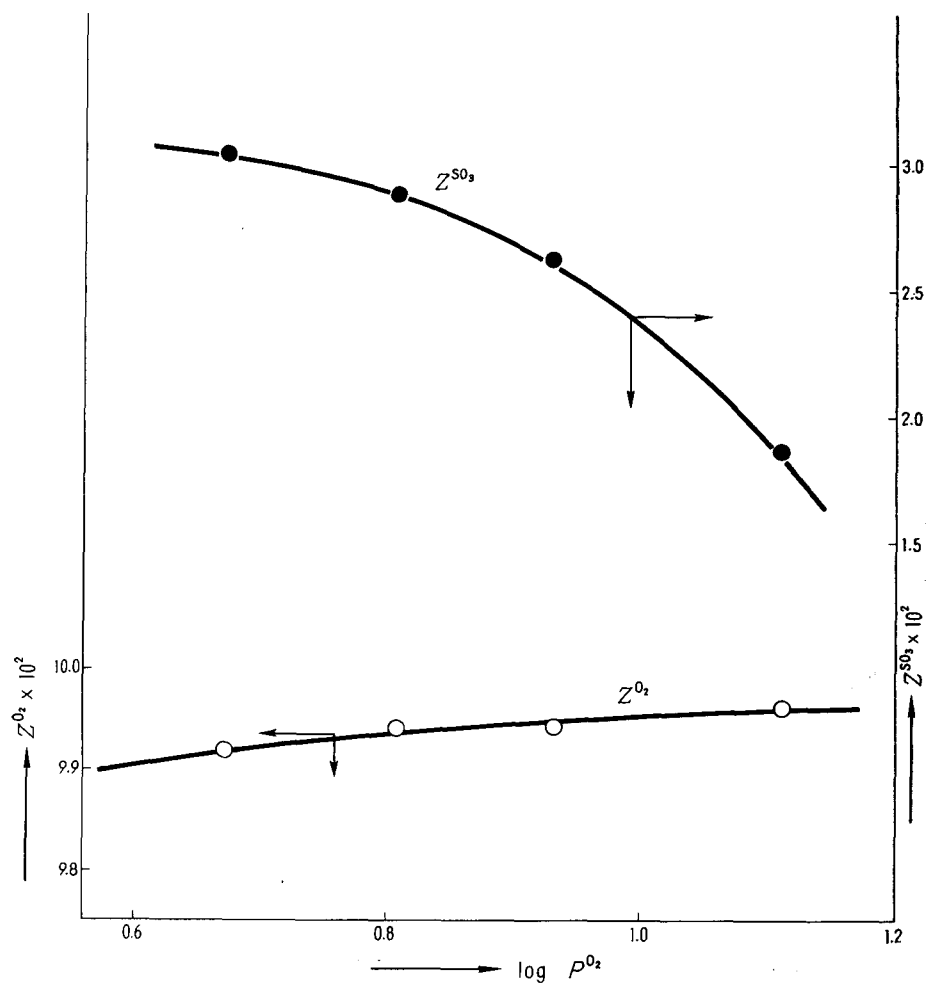


Fig. 4. Atomic fraction of ^{18}O , Z^{O_2} and Z^{SO_2} vs. $\log P^{O_2}$ 395°C.

Yoshihisa KANEKO and Hideo ODANAKA

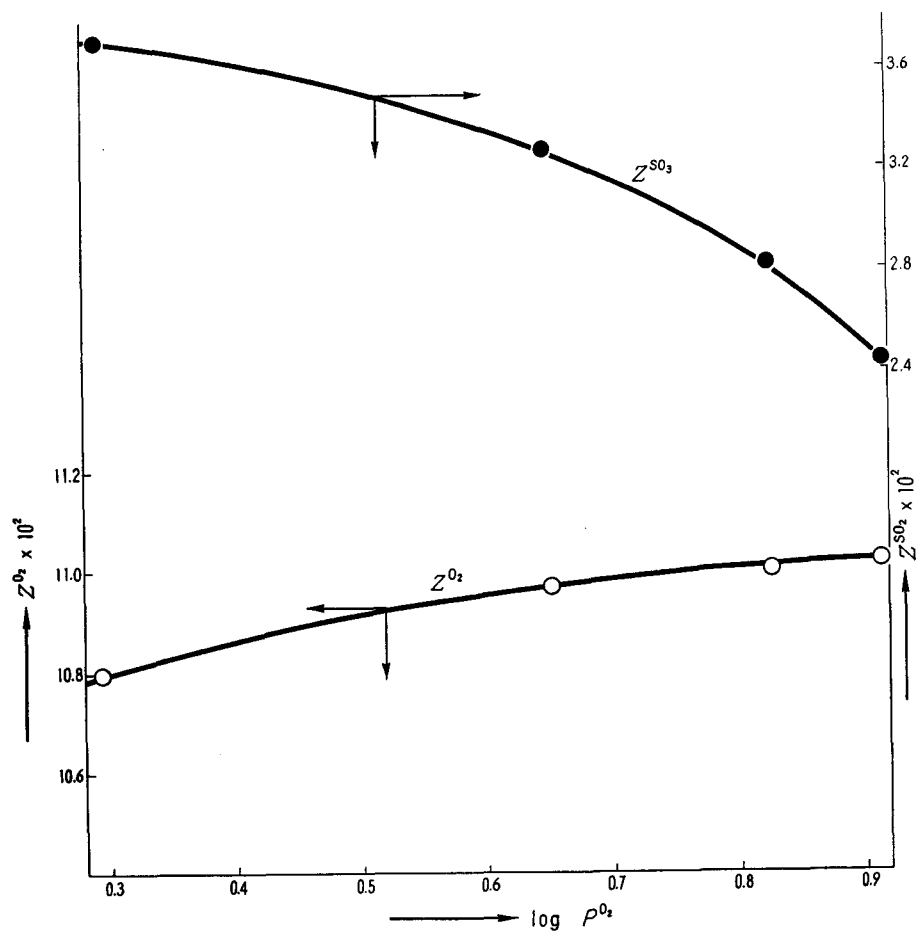


Fig. 5. Atomic fractions of ^{18}O , Z^{O_2} and S^{SO_3} vs. $\log P^{O_2}$, 405°C.

On the Mechanism of the Oxidation of Sulfur Dioxide, Part II

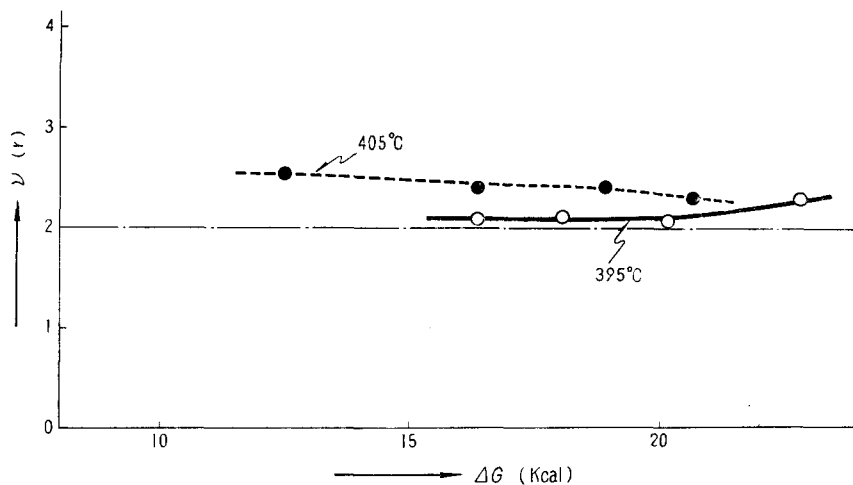


Fig. 6. Stoichiometric number $\nu(r)$ of rate-determining step vs. affinity.

Acknowledgment

The present authors wish to thank Professor Emeritus Juro HORIUTI and Professor Koshiro MIYAHARA for their kind advices and valuable discussion on the present work.

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