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ON THE MECHANISM OF THE OXIDATION OF SULFUR DIOXIDE PART I

Determination of the Stoichiometric Number by means of ^{35}S

By

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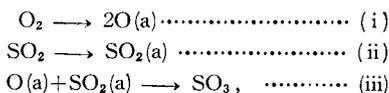
Abstract

Stoichiometric number of the rate-determining step of catalyzed oxidation of SO_2



in the presence of Pt catalyst was determined at 424°, 430° and 440°C by following the reaction up to equilibrium by observing β -ray count of ^{35}S in SO_2 and SO_3 and their partial pressures and by determining the equilibrium constant.

The stoichiometric number $\nu(r)$ was found 2. It follows from the result that the rate-determining step is one of last two steps of the sequence,



provided that the reaction followed the sequence.

The present result is in agreement on the one hand with the $\nu(r)$ -value derived from the data of REITER⁷⁾ incorporated with that of KNIETSCH¹⁰⁾ at 600°C in equilibrium and on the other hand with the conclusion arrived at previously by BORESKOV¹¹⁾.

I. Introduction

It has generally been accepted that the observation of stoichiometric number provides a powerful method of determining the mechanism of chemical reaction¹⁻⁵⁾.

The present work is concerned with the determination of the stoichiometric number of rate-determining step of catalytic oxidation of sulfur dioxide to sulfur trioxide, *i. e.*



in the presence of platinum catalyst. Assuming that reaction (1) proceeds

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through the sequence of steps,



and



we see that the stoichiometric numbers of steps (A), (B) and (C) are respectively 1, 2 and 2. According to the theory of steady reaction, the stoichiometric number $\nu(\mathbf{r})$ of rate-determining step is expressed as²⁾

$$\nu(\mathbf{r}) = -\Delta F / RT \ln (V_+ / V_-), \quad (2)$$

where V_+ or V_- is the forward or backward unidirectional rate of the overall reaction at the steady state, $-\Delta F$ its affinity and the other notations are of usual meanings.

It has now been found experimentally that the stoichiometric number of rate-determining step of reaction (1) is 2 at *ca.* 1/2 atm total pressure in the temperature range from 424 to 440°C. Principle of the determination of $\nu(\mathbf{r})$, experimental procedures and results are described in what follows.

II. Determination of $\nu(\mathbf{r})$

Eq. (2) is developed as below for the practical determination of $\nu(\mathbf{r})$. The ΔF 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 as²⁾

$$-\Delta F = RT \ln \left\{ (P^{\text{SO}_2})^2 P^{\text{O}_2} \cdot K / (P^{\text{SO}_3})^2 \right\}. \quad (3)$$

The V_- in (2) is now connected as follows with the rate of transfer of ³⁵S from sulfur dioxide to sulfur trioxide, provided that the isotopic effect on V_+ and V_- is ignorable and ³⁵S atoms are transferred in either direction only through reaction (1); the rate of transfer of ³⁵S from sulfur dioxide to sulfur trioxide is then expressed either as $-d(n^{\text{SO}_2} Z^{\text{SO}_2})/dt$ or as $2(Z^{\text{SO}_2} V_+ - Z^{\text{SO}_3} V_-)$, hence

$$-d(n^{\text{SO}_2} Z^{\text{SO}_2})/dt = 2(Z^{\text{SO}_2} V_+ - Z^{\text{SO}_3} V_-), \quad (4)$$

where Z^{SO_2} and Z^{SO_3} are the atomic fraction of ³⁵S in sulfur dioxide and in sulfur trioxide respectively and n^{SO_2} is the number of moles of sulfur dioxide in the reaction system. The coefficient 2 on the right side of (4) cares for the number of sulfur atoms thus transferred by every act of reaction (1). Since Z^{SO_2} and Z^{SO_3} are proportional to the specific β -ray counts C^{SO_2} or C^{SO_3} of ³⁵S in sulfur dioxide or sulfur trioxide respectively, we have from (4)

$$d(n^{\text{SO}_2} C^{\text{SO}_2})/dt = 2(C^{\text{SO}_3} V_- - C^{\text{SO}_2} V_+). \quad (5)$$

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The overall rate of reaction (1) is written as

$$V = V_+ - V_- = -1/2 \cdot dn^{\text{SO}_2}/dt. \quad (6)$$

Eliminating V , V_+ , V_- and ΔF from (2), (3), (5) and (6), we have

$$\nu(r) = \frac{\log \{(P^{\text{SO}_2})^2 P^{\text{O}_2} K / (P^{\text{SO}_3})^2\}}{\log \{1 - (C^{\text{SO}_3} - C^{\text{SO}_2}) d \ln P^{\text{SO}_2} / dC^{\text{SO}_2}\}}. \quad (7)$$

The stoichiometric number $\nu(r)$ of reaction (1) is now determined according to (7) by observing the quantities K , P^{SO_2} etc. on the right side of (7) in course of the progress of reaction (1).

III. Materials

Sulfur dioxide; "First grade" reagent of Na_2SO_3 from Koso Chemical Co. Ltd., Tokyo was decomposed by concentrated sulfuric acid; gas evolved was washed with conc. sulfuric acid, condensed with liquid nitrogen bath and non-condensable gas evacuated. The condensed gas was now distilled three times from -80°C to liquid nitrogen temperature in order to remove the last trace water, which upset the experiment by forming sulfuric acid with sulfur trioxide. Final sample thus purified was about one ninth of the original in volume. Oxygen; "First grade" reagent of KMnO_4 from the same company was thermally decomposed and the evolved gas purified by repeating twice the fractional distillation, reserving the first three fourth in each time as distillate. Sulfur trioxide: Sulfur trioxide was distilled from "First grade" reagent of 50% fuming sulfuric acid from the same company directly into the reaction system. Radioactive sulfur dioxide: Sulfuric acid containing ^{35}S from COMMISARAT A L'ENERGIE ATOMIQUE, France was converted into barium sulfate by a usual method. The 1:1.6-mixture of ^{35}S containing barium sulfate and dried red phosphorous was burnt in a stream of oxygen according to JOHNSON'S method⁶. Radioactive sulfur dioxide thus obtained was purified by distilling once from -80°C to liquid nitrogen temperature reducing the quantity of sample to one third of the original.

Platinum catalyst: 10.2 gm platinum gauze of 0.1 mm diameter wire from TOKURIKI & Co. Ltd., Tokyo was electrolytically platinized freshly for every series of experiments respectively conducted at 440°C , 430°C and 424°C .

IV. Apparatus

(i) Reaction System.

Fig. 1 shows the reaction system including reactor R of 2.5 cm diameter

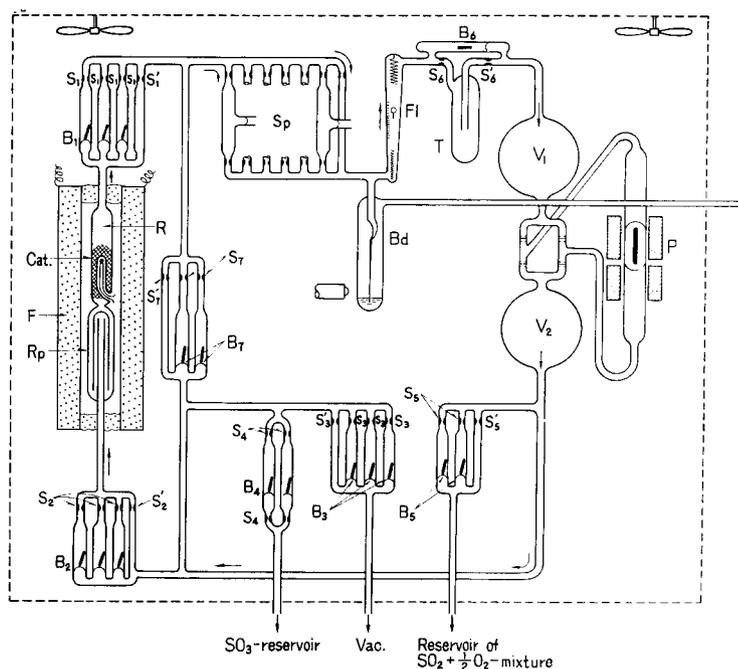


Fig. 1. Reaction system

R: Reactor	Fl: Flow meter
Cat: Catalyst	Sp: Sampling tubes
Bd: BOURDON's gauge	P: Circulating pump
F: Electric furnace	V ₁ , V ₂ : Glass vessels
T: Trap	B ₁ ...B ₇ : Breakable joints
S ₁ ...S ₇ , S' ₁ ...S' ₇ : constrictions	

glass tube with catalyst bed, *i.e.* a pack of platinized platinum gauze mentioned in III of 6 cm height. F is an electric furnace with a thermojunction in a blind tube, preliminarily calibrated at the boiling point of pure sulfur and inserted in the catalyst bed as illustrated in Fig. 1. The temperature of the catalyst was kept constant within 0.5°C by combining the junction with a thermoregulator of the electric furnace. P is a pump with which reacting gas is circulated through the circuit of the reaction system. R_P is a triply folded glass tube through which the reacting gas is preheated. Bd is a BOURDON's gauge, with its needle dipped in vacuum oil to prevent its vibration caused by the operation of pump P. Fl is a flow meter consisting of glass spring, glass float and conical glass tube (1.5 or 1.0 cm diameter at its upper or lower end respectively). Sampling tubes Sp's with breakable joints are set in parallel with each other in the circuit. Flask V₁ and V₂ are respectively of one liter

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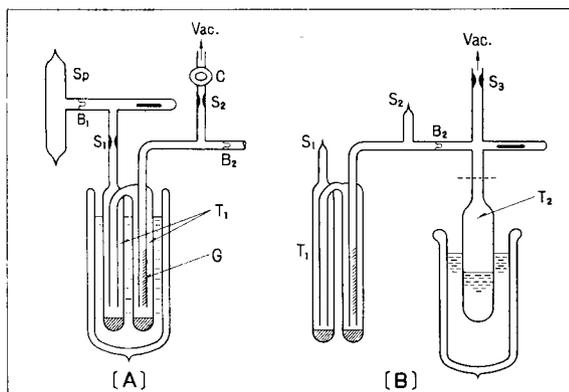


Fig. 2. Apparatus for separation SO_2 and SO_3

Sp: Sampling tube	G: Glass wool
T_1 : Trap	S_1, S_2, S_3 : Constrictions
T_2 : Glass vessel	B_1, B_2 : Breakable joint

volume, which provide the reaction system with an appropriate capacity of 4.1 liter. B_1, \dots, B_7 are breakable joints, and S_1, \dots, S_7 are constrictions for sealing.

The reaction system is kept at 90°C in order to prevent the adsorption or condensation of the reacting gas on the glass wall.

(ii) Apparatus for Separation of SO_2 and SO_3 .

Fig. 2 shows the apparatus for separation of SO_2 and SO_3 from the sampled gas. Sp is a sampling tube, T_1 a trap, G glass wool, S_1, S_2 and S_3 are constrictions for sealing and B_1 and B_2 breakable joints.

(iii) β -ray counter.

The KAKEN (the Institute of Physical and Chemical Research, Tokyo) NO. 57071 Scintillation Counter was used for β -ray count.

V. Experimental Procedure

Experiments of **Oxidation** and **Decomposition** described below have been conducted consecutively at each temperature of 440° , 430° and 424°C . **Oxidation** and **Decomposition** conducted at each temperature will be called a series of experiment. Procedures of **Oxidation**, **Decomposition** and **Separation** of SO_2 and SO_3 from samples of gas in Sp's to determine the β -ray counts of ^{35}S in the components are described below respectively under the headings **Oxidation**, **Decomposition** and **Separation**.

Oxidation; Mixture of sulfur trioxide, sulfur dioxide, radioactive sulfur dioxide and oxygen was circulated through the catalyst bed in the reaction

system, and the total pressure and β -ray counts of sulfur dioxide mixed with radioactive one and of sulfur trioxide in the reaction system were followed with time in course of the reaction as follows.

Keeping the temperature of the reactor at 450°C and that of the other parts of the reaction system A at 90°C, the whole system was evacuated through constriction S'_3 and S'_5 up to 10^{-5} mmHg. Constrictions S'_3 and S'_5 were sealed to shut off A from the vacuum line and then S'_1 and S'_2 sealed to isolate the reactor from the other parts of A. One of the breakable joints B_5 's was now opened, a recorded amounts of the 1:2 mixture of oxygen and sulfur dioxide mixed with radioactive one was admitted into A and the one of constrictions S_3 's communicated with the opened one of B_5 's was sealed off. Sulfur trioxide was now allowed to expand into A by opening one of the B_4 's, keeping the pressure outside higher than inside to prevent a backward flow, and the constrictions S_4 's above and below the opened one of B_4 's were sealed off. The gases thus admitted were mixed by circulating them for half an hour by means of P.

The temperature of the reactor was now adjusted to the desired one of the reaction, S'_7 was sealed, one of B_1 's and one of B_2 's were opened and the gas mixture was circulated through the reactor, the resulting pressure change being followed with time by BOURDON's gauge Bd. Sulfur trioxide and sulfur dioxide mixed with radioactive one in the reaction system are denoted by SO_3 and SO_2 respectively in what follows.

Sampling tubes Sp 's were sealed off successively along with the progress of the oxidation toward the equilibrium. The SO_2 and SO_3 were separated from the sampled gas, converted respectively into $BaSO_4$ as described below, and the β -ray count of ^{35}S of the respective samples of $BaSO_4$ was measured. As the equilibrium was attained, T was immersed in liquid nitrogen, the gas being circulated meanwhile. T containing condensed SO_2 and SO_3 was now sealed off by the constrictions S_6 and S'_6 . The reaction system was then evacuated by opening both bypass B_6 and one of B_3 's up to 10^{-5} mmHg to provide for the **Decomposition**.

Decomposition; Sulfur trioxide was circulated in the reaction system and the total pressure finally attained was determined to establish the value of the equilibrium constant K at each temperature as follows.

The amount of sulfur trioxide admitted was equal in moles to the sum of those of SO_2 and SO_3 in the preceding **Oxidation** at the same temperature. The total pressure in equilibrium should equal that in the preceding **Oxidation**, since the number of moles of oxygen used in the latter experiment was half as much as that of SO_2 .

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Separation; Two traps T_1 each containing 5 ml of 0.1 N HCl solution were fused to the sampling tube Sp as shown in Fig. 2 (A), immersed in liquid nitrogen and evacuated to 10^{-5} mmHg for 30~40 min. Tap C was now closed, breakable joint B_1 opened and SO_2 and SO_3 in the sampling tube were condensed in T_1 . Opening tap C, residual gas in the space below tap C was purged down to 10^{-4} mmHg. T_1 was now removed from the vacuum line by sealing off S_1 and S_2 , shaken for a while to allow HCl solution to absorb SO_2 and SO_3 at room temperature. T_1 was now fused to T_2 which contains 25 ml of 0.2 N NaOH solution, as shown in Fig. 2 (B). T_2 was immersed in liquid nitrogen and evacuated for half an hour. S_3 was now sealed off and B_2 opened. The content of T_1 kept at $70^\circ C$ was distilled into T_2 cooled by liquid nitrogen, which was completed without pumping within about three hours leaving a small amount of liquid in T_1 . T_2 was cut off at the dotted line in Fig. 2 (B), bromine water poured in and the resulting solution was filtered in order to remove pieces of glass in it. The residue on the filter was washed with pure water, and the wash was added to the filtrate, SO_4^{2-} in the filtrate was converted into $BaSO_4$, weighed and its specific β -ray count C^{SO_2} was determined from the β -ray count of the $BaSO_4$ and its weight by a usual method⁷⁾.

SO_4^{2-} in the residual liquid in T_1 was similarly converted into $BaSO_4$, weighed and its specific β -ray count C^{SO_3} determined. The ratio r of the weight of $BaSO_4$ from SO_2 to that from SO_3 gives the ratio of the number of moles of SO_2 to that of SO_3 . Partial pressure P^{SO_2} of SO_2 and that P^{SO_3} of SO_3 were determined from the observed total pressure P as $P^{SO_2} = P/(3/2 + r)$ and $P^{SO_3} = P/r(3/2 + r)$.

It has been confirmed by control experiments that sampled SO_2 and SO_3 were thus separated quantitatively and that exchange of ^{35}S between SO_2 and SO_3 did not take place without the catalyst within experimental error.

IV. Result

The results of **Oxidation** and **Decomposition** consecutively conducted at each temperature of 440° , 430° and $424^\circ C$ are summarized in Tables 1 to 3. "Time of reaction" is the time elapsed from the beginning of the circulation of gas mixture through the catalyst bed until the sampling.

Figs. 5 to 7 shows the plots of C^{SO_2} and C^{SO_3} against $\log P^{SO_2}$ at 440° , 430° and $424^\circ C$ respectively, from which the values of $d \ln P^{SO_2} / dC^{SO_2}$ have

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TABLE 1. Series of Experiments at 440°C
Series (i) SO₂ oxidation

Time of reaction hr	Total pressure cm Hg	P_{SO_2} cm Hg	P_{SO_2} cm Hg	C^{SO_2} c.p.m.mg ⁻¹	C^{SO_2} c.p.m.mg ⁻¹
0	33.55	10.60	15.30	264	0
4.3	32.15	13.40	12.50	263	57
9.8	30.90	15.90	10.10	261	90
27.8	28.15	21.40	4.51		
55.8	26.80	24.10	1.80		
59.8	26.75	24.20	1.70		
66.0	26.74	24.22	1.68		
69.0	26.74	24.22	1.64		

Series (ii) SO₃ decomposition

Time of reaction hr	Total pressure cm Hg	P^{SO_3} cm Hg	P^{SO_2} cm Hg
0	25.90	25.90	0
48	26.70	24.30	1.61
58	26.70	24.30	1.61

been determined with the aid of prism^{8),*)} The stoichiometric number $\nu(r)$ of the rate-determining step is now determined according to (7) at several values of ΔF from the values of $d \ln P^{SO_2}/dC^{SO_2}$ thus determined and the contemporaneous values of C^{SO_2} and C^{SO_2} . Fig. 8 shows $\nu(r)$ thus determined plotted against the affinity ΔF .

*) It may be seen as below that the successive sampling does not affect the value of $d \ln P^{SO_2}/dC^{SO_2}$ or, in other words, its value actually observed by sampling equals what would result without sampling.

We have identically

$$\frac{d \ln P^{SO_2}}{dC^{SO_2}} = \frac{dP^{SO_2}/dt}{P^{SO_2}} \bigg/ \frac{dC^{SO_2}}{dt}$$

The sampling excludes now partially the volume of **A** and its content by the same fraction less than 1%. This varies the numerator and the denominator of the right side of of the above equation by the same factor, admitted that the rate of oxidation or that of ³⁵S transfer remains respectively the same at a given partial pressure P^{SO_2} of SO₂, which uniquely defines the total pressure and the composition of the gas mixture under the condition of the present experiment. It follows that the left side of the above equation remains the same function of P^{SO_2} , hence $d \ln P^{SO_2}/dC^{SO_2}$ is not affected by the sampling, although the numerator and the denominator of the right side varies individually.

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TABLE 2. Series of Experiments at 430°C
Series (i) SO₂ oxidation

Time of reaction hr	Total pressure cm Hg	P^{SO_3} cm Hg	P^{SO_2} cm Hg	C^{SO_2} c.p.m.mg ⁻¹	C^{SO_3} c.p.m.mg ⁻¹
10	37.40	8.45	18.40	302	0
12	35.95	11.35	15.50	—	—
32	33.70	15.85	11.00	—	—
56	32.05	19.15	7.70	293	180
84	31.04	21.20	5.64	289	184
107	30.41	22.40	4.44	285	193
130	30.01	23.21	3.61	282	195
170	29.52	24.19	2.65	—	—
326	28.62	25.90	0.95	—	—
361	"	"	"	—	—
391	"	"	"	—	—

Series (ii) SO₃ decomposition

Time of reaction hr	Total pressure cm Hg	P^{SO_3} cm Hg	P^{SO_2} cm Hg
0	28.21	26.90	0
240	28.60	26.02	0.90
335	28.63	25.91	0.90
372	28.60	26.00	0.92

It may be concluded from the result in Fig. 8 that the stoichiometric number $\nu(r)$ of reaction (1) is 2 in the present experimental condition.

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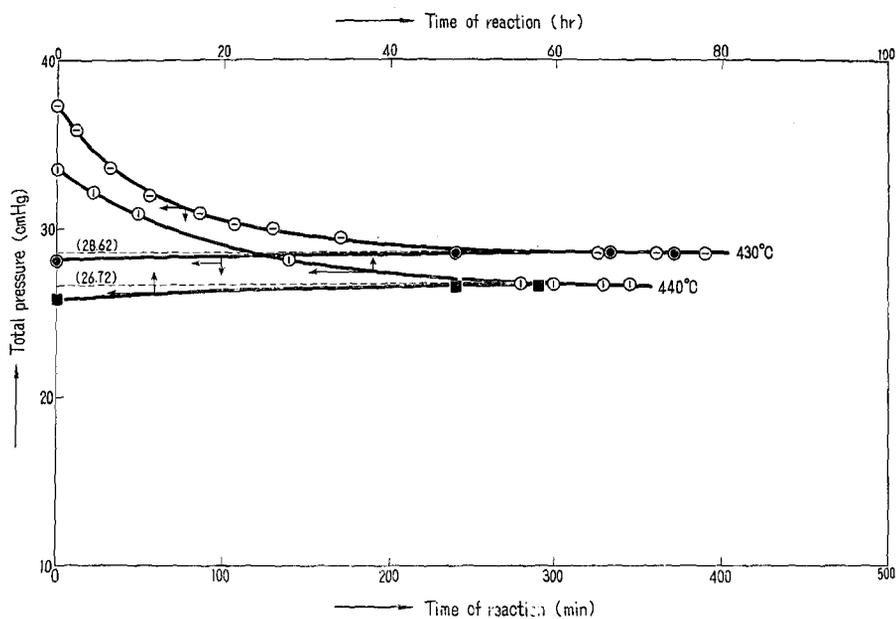


Fig. 3. Total pressure vs. time of reaction
 ○ or ⊖ shows the total pressure at 440° or 430°C observed by
Oxidation experiments (cf. V)
 ■ or ● shows the total pressure at 440° or 430°C observed by
Decomposition experiments (cf. V)
 Horizontal broken lines indicate the total pressure finally attained.

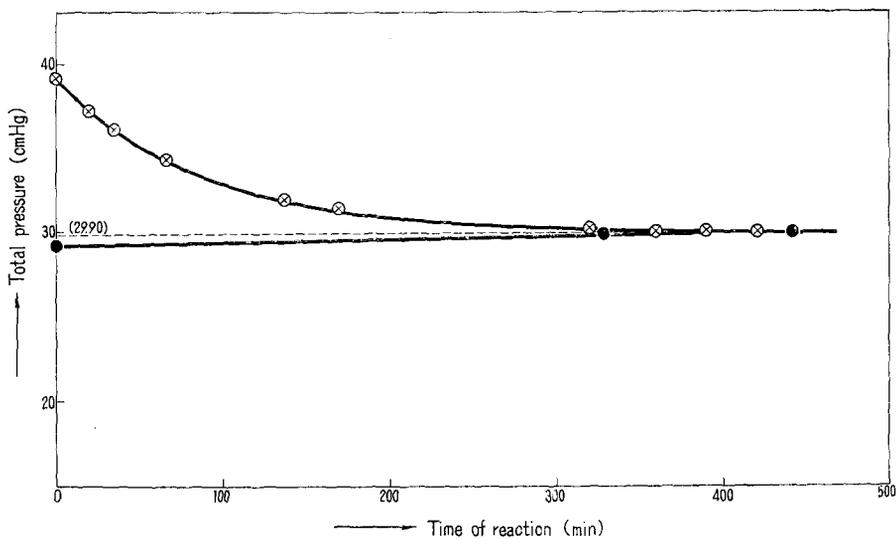


Fig. 4. Total pressure vs. time of reaction
 ⊗ or ● shows the total pressure observed at 424°C by
Oxidation experiments (cf. V) or **Decomposition**
 experiment respectively.
 Horizontal broken line shows the total pressure
 finally attained.

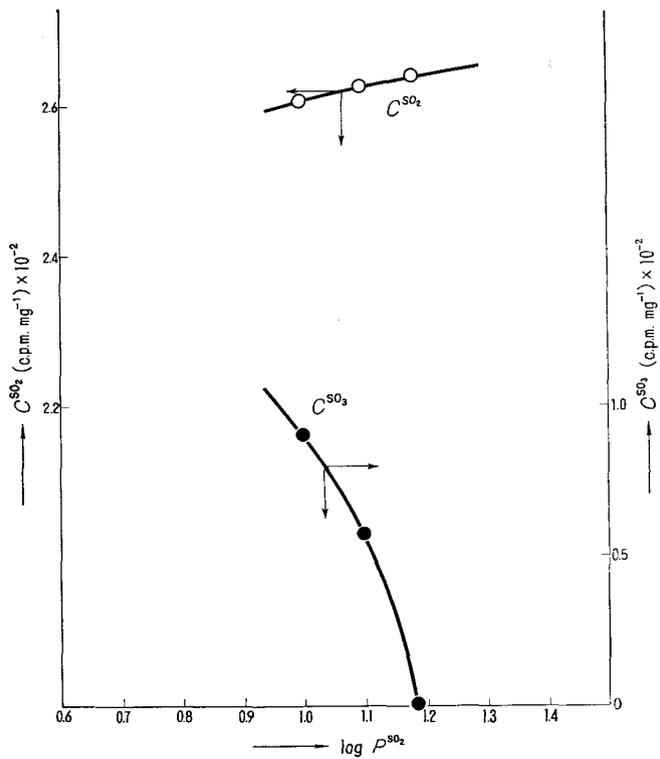


Fig. 5. C^{SO_2} and C^{SO_3} vs. $\log P^{SO_2}$, 440°C.

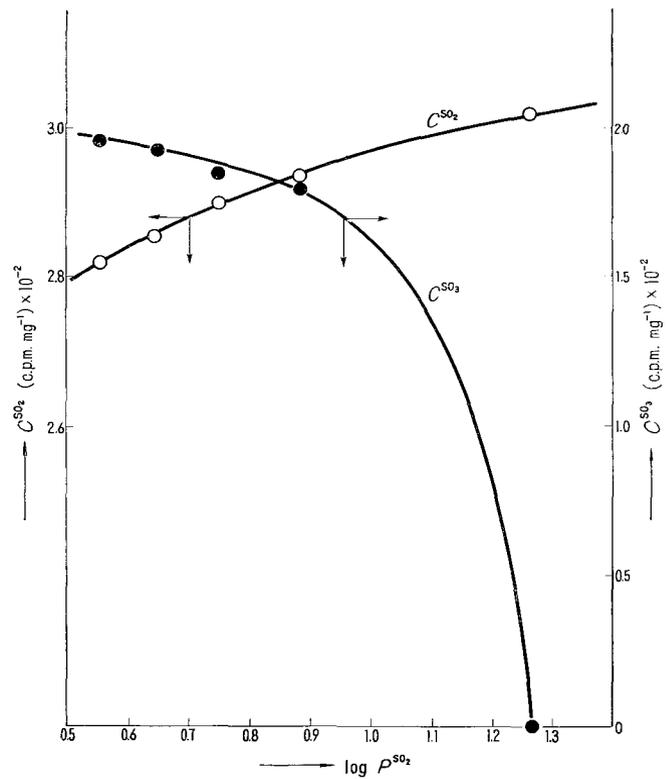


Fig. 6. C^{SO_2} and C^{SO_3} vs. $\log P^{SO_2}$, 430°C.

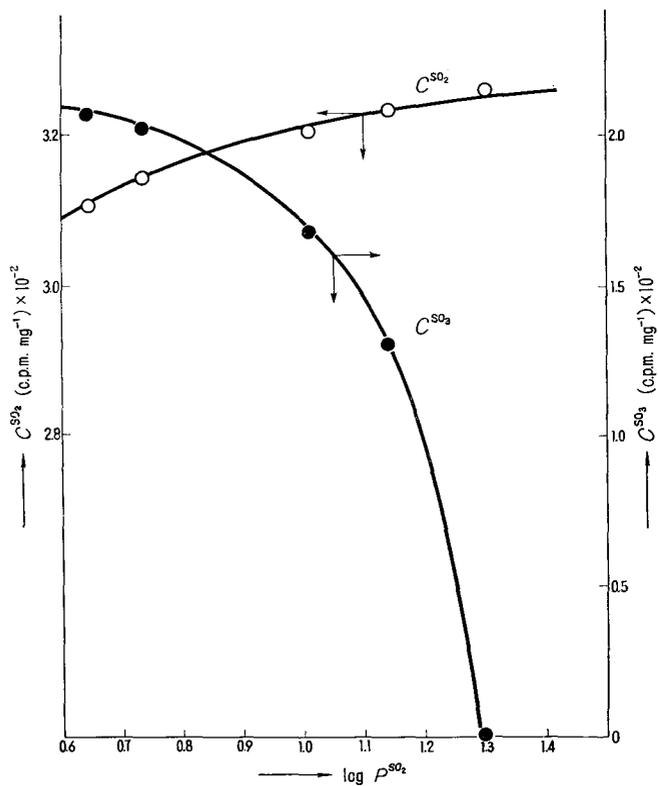


Fig. 7. C^{SO_2} and C^{SO_3} vs. $\log P^{SO_2}$, 424°C.

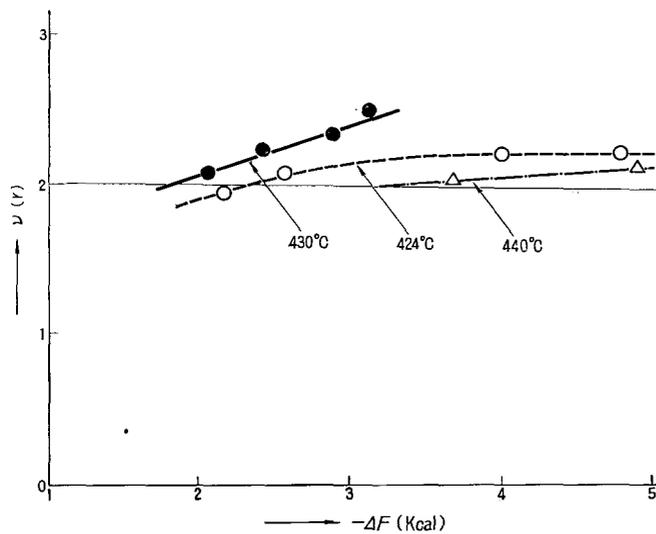


Fig. 8. $\nu(r)$ vs. Affinity.

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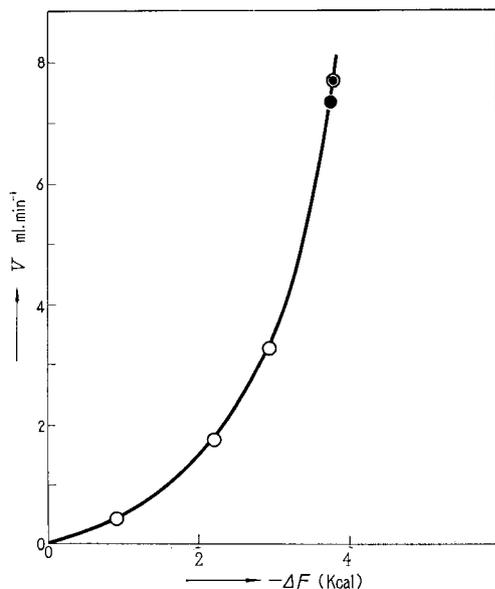


Fig. 9. V vs. ΔF .

- REITER's value ○ KNIETSCH's value.
 ⊙ KNIETSCH's value adjusted to REITER's one.

VII. REITER'S Experiment

REITER⁹⁾ has observed the unidirectional rate in equilibrium of reaction (1) by means of ³⁵S, in the presence of Pt-catalyst over the temperature range from 600° to 674°C. He measured also the overall rate V of the oxidation over the temperature range from 420° to 600°C quite off from equilibrium.

The unidirectional rate $V_{+,e}$ in equilibrium allows us to determine in accordance with the equation²⁾

$$\nu(r) = - \frac{V_{+,e}}{RT \left\{ \frac{\partial V}{\partial (\Delta F)} \right\}_e}, \quad (8)$$

whereas the value $\left\{ \frac{\partial V}{\partial (\Delta F)} \right\}_e$ of $\frac{\partial V}{\partial (\Delta F)}$ in equilibrium is not available from REITER's result. However, KNIETSCH¹⁰⁾ observed V early as a function of ΔF up to the neighbourhood of equilibrium at 600°C in the presence of platinum catalyst. Fig. 9 illustrates the relation observed by KNIETSCH, where the scale of V is changed so as to identify his data of V at $-\Delta F = 3.82$ Kcal numerically with that measured by REITER at the same value of $-\Delta F$. The V is thus given as a function of ΔF up to equilibrium in REITER's scale, on

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TABLE 3. Series of Experiments at 424°C
Series (i) SO₂ oxidation

Time of reaction hr	Total pressure cm Hg	P_{SO_3} cm Hg	P_{SO_2} cm Hg	C_{SO_2} c.p.m.mg ⁻¹	C_{SO_3} c.p.m.mg ⁻¹
0	39.11	9.41	19.81	326	0
19	37.19	13.19	16.00	—	—
35	36.10	15.40	13.79	323	131
66	34.28	18.99	10.20	320	169
137	31.91	23.81	5.41	314	202
169	31.39	24.79	4.40	311	204
320	30.10	27.40	1.82	—	—
355	29.90	27.80	1.41	—	—
390	"	"	"	—	—
420	"	"	"	—	—

Series (ii) SO₃ decomposition

Time of reaction hr	Total pressure cm Hg	P_{SO_2} cm Hg	P_{SO_3} cm Hg
0	29.21	0	29.21
328	29.88	1.40	27.78
441	"	1.40	"

which base REITER's value of $V_{+,e}=0.85$ ml/min. is given. The value of $\{\partial V/\partial \Delta F\}_e$ is thus obtained in REITER's scale from the inclination of the tangent to the curve in Fig. 9 at $\Delta F=0$, as 2.3×10^{-2} ml/min. cal. Combining this value of $\{\partial V/\partial (\Delta F)\}_e$ with the above value of $V_{+,e}$, $\nu(r)$ is calculated at 1.8 in accordance with (8), in agreement with the present result over the temperature range from 424° to 440°C.

VIII. Discussion

It follows from $\nu(r)=2$ of reaction (1) that the rate-determining step is either (B) or (C) but not (A), if the reaction followed the sequence. REITER⁹⁾ concluded from his experimental result under some kinetic assumption that the rate-determining step can not be (A), which is in conformity with the present result as well as the conclusion derived by incorporating his result with the KNIETSCH's data without any kinetic assumption.

BORESKOV¹¹⁾ has introduced the concept of molecularity m , *i. e.* the number of chemical species involved in the rate-determining step, which is determined as

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$$m = \frac{E_2 - E_1}{Q}; \quad (9)$$

E_1 or E_2 is the activation energy of the forward or backward unidirectional reaction and Q is the heat of reaction in accordance with the chemical equation, where the coefficient of the chemical species in question is normalized to unity, *e. g.* as $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$ with the coefficient of SO_2 normalized to unity. He thus determined $m=1$ for SO_2 from the values of E_1 , E_2 and Q observed by TAYLOR¹²⁾ in the presence of Pt catalyst over the temperature range from 665° to 700°C. This conclusion states in terms $\nu(r)$ that $\nu(r)=2$ as referred to the chemical equation (1).

We have seen so far that $\nu(r)$ measured experimentally by the present author under the condition off and in equilibrium throughout at temperatures from 424° to 440°C agrees with the conclusion of BORESKOV¹¹⁾ near 700°C as well as that derived from the incorporated results of REITER⁹⁾ and KNIETSCH¹⁰⁾ in equilibrium at 600°C, which suggests that the same mechanism is operative over the temperature range from 400° to 700°C under the condition off and in equilibrium throughout.

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