JOURNAL OF CATALYSIS **10**, 1-12 (1968)

The Mechanism and the Kinetics of Sulfur Dioxide Oxidation on Catalysts Containing Vanadium and Alkali Oxides

P. MARS* AND J. G. H. MAESSEN

From the Central Laboratory, Staatsmijnen/DSM, Geleen, Netherlands

Received June 22, 1967; revised September 18, 1967

In continuation of a previous study on a catalyst containing potassium and vanadium oxides, it is shown that the oxidation of SO_2 on a *sodium*-potassium-vanadium catalyst also proceeds via rapid establishment of the equilibrium, $SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}$ (equilibrium constant K) and that the reaction of oxygen with V^{4+} is the rate-determining step. On the basis of this finding it has been derived that the reaction rate can be formulated as follows

$$v = kp_{O_2} \frac{Kp_{SO_2}/p_{SO_3}}{[1 + (Kp_{SO_2}/p_{SO_3})^{1/2}]^2}$$

By means of isothermal and differential kinetic measurements on both types of catalysts mentioned above this expression has been checked and found correct. The value of the equilibrium constant K calculated from the kinetic experiments is in good agreement with that derived from analytical determinations.

I. INTRODUCTION

Since the time when the platinum catalysts in the sulfuric acid industry were superseded by vanadium-containing masses (1920–1930), there has been a continuous stream of publications dealing with the kinetics of the process. The object of these studies was, on the one hand, to place the design of sulfuric acid plants on a more exact basis and to provide a key to the optimization of industrial reactor performance (atmospheric pollution) and, on the other, to gather information on the mechanism of the reaction. Unfortunately, many of the papers that have so far been published on these measurements again and again disclosed new kinetic formulations. In Table 1 the most important results are summarized. The results show that most authors consider the reaction to be approximately first order (*3*, *4*, *7*, *10*, *12*) with respect to oxygen; with respect to SO_2 the reaction order is in between one-half and one (*1*, *2*, *3*, *7*, *11*). In the absence of SO_3, however (thus, at the start of the reaction), SO_2 has only a minor effect on the reaction rate. This is evident from the study by Boreskov, Ritter, and Volkova (*5*), whose results are illustrated in Fig. 1. These workers recorded the temperature at which a given slight heat generation took place in a reactor during the passage of SO_2–O_2 mixtures of strongly varying concentration over a potassium-vanadium catalyst.

All investigators share the opinion that the reaction rate is slowed down by even small amounts of SO_3. As this effect is already noticeable far from chemical equilibrium, its cause must obviously be sought in the reaction mechanism.

As appears from Table 1, there is quite some diversity of opinion as to the details of the kinetics. One of the principal causes is undoubtedly the insufficient control of the catalyst temperature. In the fast and highly exothermic reactions involved here, this temperature may considerably exceed that of the gas or the reactor wall. The kind of the error in the reaction rates found depends on the location of the point where

---

* Present address: Technical University Twente, Enshede, Netherlands.

TABLE 1

LITERATURE DATA ON THE KINETICS OF THE SO_2 OXIDATION ON VANADIUM OXIDE CATALYSTS PROMOTED WITH ALKALI METAL

Author and reference	Experimental data and catalyst	Kinetic data	Notes
G. K. Boreskov and V. P. Pligunov (*1*)	Reaction on $2SnO_2 \cdot K_2O \cdot BaO \cdot V_2O_5 \cdot 8SiO_2$	$v = k \frac{p_{SO_2} - p_{SO_2,eq}}{(p_{SO_3})^{1/2}}$	
G. K. Boreskov (*2*)	Reaction in flowing system, temp. >440°C, on barium tin vanadate	$v = k \frac{p_{SO_2}}{\sqrt{(p_{SO_3})^{1/2}}}$	
G. K. Boreskov and F. J. Sokolova (*3*)	Reaction temperature, 470°C Catalyst: $2K_2O \cdot BaO \cdot 0.5Al_2O_3 \cdot V_2O_5 \cdot 12SiO_2$ Degree of conversion, 21–91% SO_2 concentration, 4–23% O_2 concentration, 6.5–40%	$v = kp_{O_2} \left(\frac{p_{SO_2}}{p_{SO_3}} \right)^{0.8}$	
K. J. Brodovich (*4*)	—	Reaction rate proportional to p_{O_2}	
G. K. Boreskov, L. G. Ritter, and E. J. Volkova (*5*)	The temperature at which the catalyst reaction rate becomes perceptible is determined in gas mixtures with 7–95% SO_2 and 5–75% O_2 on vanadium oxide containing potassium and barium.	If SO_3 is absent only p_{O_2} has an influence on the reaction rate	See Fig. 1
P. H. Calderbank (*6*)	In a reactor (= 12-mm diameter bore in aluminum block furnace) the following quantities are varied: O_2 from 4% to 18%; SO_2 from 17% to 80%; gas load; temperature from 360° to 450°C. Catalyst: 12% V_2O_5 + 2% Na on silica gel. Particle diam. 1.2–1.7 mm.	$v = kp_{O_2}{}^a p_{SO_2}{}^b$ $0.72 < a < 0.85$ $0.35 < b < 0.43$	Two of the three test series were performed under conditions having a strongly reducing effect on the catalyst.
R. B. Eklund (*7*)	Differential measurements under isothermal conditions; 4–20% O_2, 1–6% SO_2, and 1–9% SO_3; 420–554°C; catalyst, V_2O_5 and K_2SO_4 on kieselguhr; $\phi_p = 0.67–1.38$ mm.	$v = kp_{O_2} \left(\frac{p_{SO_2}}{p_{SO_3}} \right)^{0.5} - \frac{k}{\overleftarrow{K}^2} \left(\frac{p_{SO_3}}{p_{SO_2}} \right)^{1.5}$	In part of the measurements the diffusion in the pores had an effect on the reaction rate.

TABLE 1 (*Continued*)

Author and reference	Experimental data and catalyst	Kinetic data	Notes
M. Goldman, L. N. Canjar, and R. B. Beckmann (*8*)	Gas flows are passed at various rates and at temperatures of 360–426°C through fluidized and fixed catalyst beds in a 33-mm diameter reactor. Catalyst: 10% V_2O_5 + 33% K_2SO_4 on silica gel.	$v = \dfrac{kp_{O_2}p_{SO_2}}{(1 + b_1p_{O_2} + b_2p_{SO_2} + b_3p_{SO_3})^2}$	
M. S. Zakar'evski and Man-Cheng Chang (*9*)	390–475°C; V_2O_5 containing potassium and sodium.	$v = kp_{SO_2}{}^{0.3}p_{O_2}{}^{0.4-1.0}$	The exponents in the rate equation vary with the reaction temperature in the way indicated.
P. B. Rzaev, V. A. Roiter, and G. P. Korneichuk (*10*)	Flow reactor with diameter 18 mm; particle size 1.5–2.0 mm. Catalyst: V_2O_5 containing barium and aluminum.	$v = kp_{O_2}(p_{SO_2}/p_{SO_3})^{0.4}$	
B. Davidson and G. Todes (*11*)	At 240–383°C in a flowing system; conversion <0.22; p_{O_2} and p_{SO_2} are varied; no preconversion; catalyst: 10% K_2O + 8.5% V_2O_5 on kieselguhr.	At 340°C: $v = k(p_{SO_2}{}^{0.87}/p_{O_2}{}^{0.5})$ At 384°C: $v = kp_{O_2}{}^{0}p_{SO_2}{}^{0.62}$	These results are somewhat remarkable compared with the others; this may be due to the very low reaction temperatures.
G. V. Boreskov, R. A. Buyanov, and A. A. Ivanov (*12*)	Differentially working circulation reactor, 485°C; p_{O_2} and p_{SO_2} have been varied; potassium-vanadium oxide catalyst.	$v = kp_{O_2}\dfrac{p_{SO_2}}{p_{SO_2} + Ap_{SO_3}} \times \left[1 - \left(\dfrac{p_{SO_3}}{p_{SO_2}p_{O_2}{}^{1/2}K_{eq}}\right)^2\right]$	

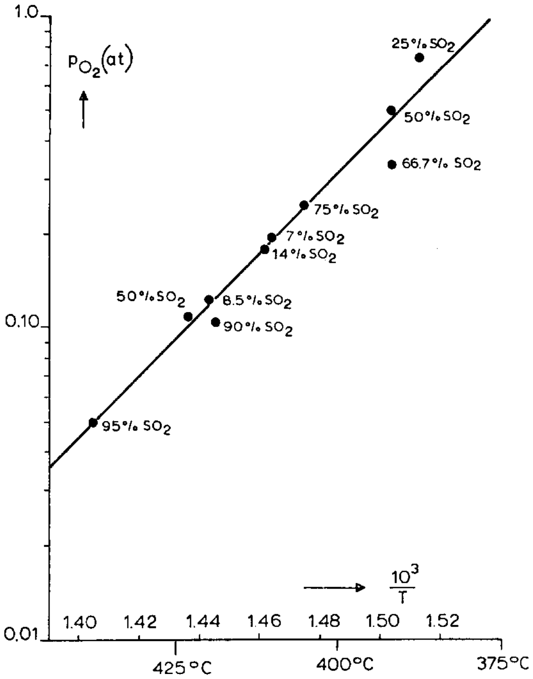

FIG. 1. Temperatures at which the reaction rate on the K and V catalyst becomes perceptible, as a function of the SO_2 and oxygen contents in the gas mixture (total pressure 1 atm). Measured by Boreskov, Ritter, and Volkova (*5*).

the temperature is measured: near the reactor wall, in the surrounding furnace space, or in the center of the catalyst bed. Once the heat transfer coefficient can be estimated, the difference between the average bed temperature and the wall temperature can be calculated from the average heat generation. In many cases this difference proves to be considerable (i.e., >25°C). Among the literature deserving further consideration the publications by Eklund (*7*), Calderbank (*6*), and Boreskov, Buyanov, and Ivanov (*12*) relate to experiments in which the temperature distribution can be regarded as sufficiently homogeneous ($\Delta T <$ 10–15°C). Besides these, the papers by Boreskov should be mentioned here. This author derived in 1937 the frequently used kinetic formula

$$v_{SO_3} = kp_{O_2}(p_{SO_2}/p_{SO_3})^n \qquad (1)$$

where $n = 0.8$. [According to Rzaev and co-workers (*10*), it would be more correct to take n equal to 0.4.]

Recently Boreskov, Buyanov, and Ivanov (*12*) described their results from differential measurements with the formula

$$v_{SO_3} = kp_{O_2}\frac{p_{SO_2}}{p_{SO_2} + Ap_{SO_3}} \qquad (2)$$

This formula reflects the above-mentioned regularities.

Eklund (*7*) did measurements under differential conditions in a reactor operated under adequately isothermal conditions. He arrived at approximately the same formulation as Boreskov, but introduced a correction for the rate of the reverse reaction (Table 1).

In a previous publication on the mechanism of the reaction involved (*13*) the present authors showed that the equilibrium between the vanadium ions dissolved in the pyrosulfate melt and the partial pressures of the sulfur oxides is always established

$$SO_2 + 2V^{5+} + O^{2-} \leftrightarrows SO_3 + 2V^{4+} \qquad (3)$$

The rate of the reaction between oxygen and V^{4+} is rate-determining for the process. On the basis of this mechanism the derivation has been given of the kinetic formula

$$v_{SO_3} = kp_{O_2}\frac{Kp_{SO_2}/p_{SO_3}}{[1 + Kp_{SO_2}/p_{SO_3})^{1/2}]^2} \qquad (4)$$

The present publication starts with a discussion of the mechanism mentioned above. Next follows a report of kinetic measurements on two catalysts and a confrontation of the results with the kinetic expression (4) as well as with the values of K derived from analytical determinations.

II. EXPERIMENTAL

The catalytic activity was measured under differential conditions in a 6-mm diameter reactor tube (volume about 20 ml) placed in a heating bath of fluidized carborundum particles. Diameters of catalyst particles were approx. 0.5 mm. For the analytical procedure we refer to an earlier publication (*13*). The maximum shift in conversion was 0.15. Minor corrections (<10%) were applied to the rate of SO_2 conversion for the extent to which the temperature of the catalyst particle may exceed that of the fluidized bed, and for minor deviations in the temperature adjustment. The excess temperature, calculated by means of the customary heat transfer relations, was found to be less than 10°C in virtually all cases. The activation energy used for these corrections was taken as 30 kcal/mole.

Estimation of the diffusion influence of reactants in gas-filled pores by means of the Thiele method showed that no diffusional retardation of the rate can be expected.

Diffusion of reactants in the catalytically active liquid film of potassium pyrosulfate (wherein vanadium oxides are dissolved) does not influence the reaction rate either, because separate experiments showed that the activity of catalysts containing less than 6% or 7% V_2O_5 is practically proportional to the percentage of active material. The compositions of the catalysts used, kindly supplied by three catalyst manufacturers, are given in Table 2.

The analytical method used for determining the equilibrium constant K was analogous to that described previously (*13*): After conditioning of the catalyst in a gas of known composition, and rapid cooling, the concentrations of V^{4+} and V^{5+} in the catalyst are determined as well as the concentrations of SO_2 and SO_3 in the gas phase.

III. The Mechanism of the Sulfur Dioxide Oxidation on Alkali-Promoted Vanadium Catalysts

Equation (3), which depicts the equilibrium between the vanadium ions in the melt and the sulfur oxides in the gas phase, can be formulated as follows:

$$K^x = \frac{p_{SO_3}}{p_{SO_2}} \frac{a^2{}_{V^{4+}}}{a^2{}_{V^{5+}}} \frac{1}{a_{O^{2-}}} \tag{5a}$$

One arrives via

$$K = \frac{p_{SO_3}}{p_{SO_2}} \frac{[V^{4+}]^2}{[V^{5+}]^2} \tag{5b}$$

at formula (4), provided the following assumptions are made: (1) $a_{O^{2-}}$ is independent of the activity of the other components; (2) the activity coefficients of V^{4+} and V^{5+} are equal; (3) the activity of V^{4+} at the surface is proportional to that in the melt. Assumptions (2) and (3) are not unlikely; assumption (1) needs some explanation.

One might conceive that this assumption is justified in view of the large excess of potassium pyrosulfate present. Professor Wagner (Göttingen), however, brought to our notice that the activity of the oxygen ions may quite well be a function of p_{SO_3} owing to the establishment of the following equilibria:

$$\begin{array}{ll} & S_2O_7^{2-} \leftrightarrows SO_4^{2-} + SO_3 \\ \text{and} & SO_4^{2-} \leftrightarrows SO_3 + O^{2-} \\ \hline \text{so} & S_2O_7^{2-} \leftrightarrows O^{2-} + 2SO_3 \end{array} \tag{6}$$

Combination with (3) gives

$$SO_2 + 2V^{5+} + S_2O_7^{2-} \leftrightarrows 3SO_3 + 2V^{4+} \tag{7}$$

Allowance being made for assumptions (2) and (3), this yields

$$K' = \frac{p_{SO_3{}^3}}{p_{SO_2}} \frac{[V^{4+}]^2}{[V^{5+}]^2} \frac{1}{a_{S_2O_7{}^{2-}}} \tag{8}$$

The problem arises whether $a_{S_2O_7{}^{2-}}$ or $a_{O^{2-}}$ may be regarded as constant. We did an extensive investigation to see if the concentration of $S_2O_7^{2-}$ in the melt is not strongly dependent on p_{SO_3}. To that end we

TABLE 2
Composition of the Catalysts[a]

Catalyst	Vanadium oxide calculated as V_2O_5 (% by wt.)	K (% by wt.)	(K + Na)/V (at./at.)	Other compounds
1	8.2	17	2.8	5.1% Ca, 0.9% Na
2	7.1	9	1.65	0.08% Ca, 0.15% Na
3	6.8	10	2.5	0.07% Ca, 2.9% Na

[a] The support of all the catalysts is silica.

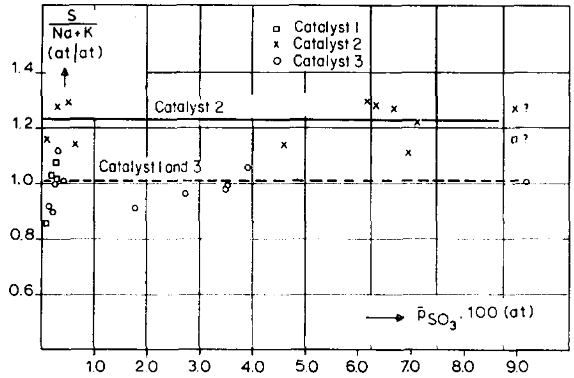

FIG. 2. Chemical composition of the catalyst; the sulfur/alkali ratio as function of the partial SO_3 pressure. Temperature: 450°C. The p_{SO_3}/p_{SO_2} ratio varies from 1/40 to 12.

determined the ratio between the total amounts of sulfur and alkali after rapid cooling of catalyst samples that had been in contact with an SO_3–SO_2–O_2 mixture for ~20 hr. Figures 2 and 3 illustrate the observations made on three industrial catalysis. They show that the above-mentioned ratio remains very close to unity and varies very slightly with temperature. Hence, the composition is virtually identical to that of pyrosulfate, so that the assumption of $a_{S_2O_7^{2-}}$ being constant would seem correct. Studies by Fraser and Kirkpatrick (*14*), Topsøe and Nielsen (*15*), and Tandy (*16*) also reveal that the composition of the melt is identical to that of pyrosulfate.

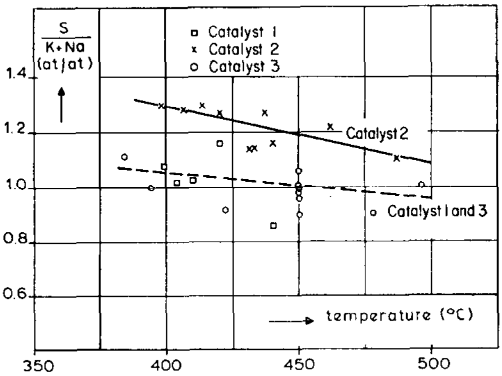

FIG. 3. Chemical composition of the catalyst; the sulfur/alkali ratio as function of the temperature. The 3.4% of Ca present in Catalyst 1 is assumed to be bounded to $CaSO_4$; the sulfur content found has been corrected accordingly; p_{SO_3} varies from 0.002 to 0.10 atm, p_{SO_3}/p_{SO_2} from 1/40 to 12.

In view of (8), one might expect

$$K'' = \frac{p_{SO_3}{}^3}{p_{SO_2}} \frac{[V^{4+}]^2}{[V^{5+}]^2}$$

to be constant. However, experiments show (see Table 3) that this is not so: calculations from test results obtained under nonequilibrium* conditions and very widely varying values of p_{SO_3} yielded strongly different values for K'', whereas K [formula (5b)] remained fairly constant.

These analytical measurements show that as demonstrated by earlier measurements the ratio between the V^{4+} and V^{5+} concentrations very largely adapts itself to that between p_{SO_3} and p_{SO_2} in the way described in Eq. (5b) (see Table 3). Allowance being made for the very large variations in the p_{SO_2}/p_{SO_3} ratio and for the experimental difficulties, the variations in K are relatively small.

IV. THE KINETIC MEASUREMENTS ON TWO ALKALI-PROMOTED CATALYSTS

1. *Influence of the Partial Pressure of Oxygen on the Reaction Rate*

The results of our experiments, in which p_{O_2} was varied are illustrated in Fig. 4. Here the reaction rate is expressed in the function v/w, where v is the reaction rate and w the term

---

* That is, there is no equilibrium between SO_2, O_2, and SO_3.

TABLE 3

Results of Measurements on Catalyst 3 Regarding the Equilibrium between the Sulfur Oxides and Vanadium Ions[a]

p_{SO_2} (10^{-2} atm)	p_{SO_3} (10^{-2} atm)	$\frac{[V^{4+}]}{[V^{5+}]}$	$\frac{p_{SO_3}}{p_{SO_2}}$	$K = \left(\frac{[V^{4+}]}{[V^{5+}]}\right)^2 \frac{p_{SO_3}}{p_{SO_2}}$	$K'' = \left(\frac{[V^{4+}]}{[V^{5+}]}\right)^2 \frac{p_{SO_3}^3}{p_{SO_2}}$
3.97	0.26	3.52	0.0655	0.81	5.6×10^{-6}
1.57	2.72	1.02	1.73	1.82	1.35×10^{-3}
0.68	3.49	0.605	5.14	1.88	2.3×10^{-6}
3.59	0.43	2.78	0.121	0.93	1.7×10^{-5}
0.67	3.57	0.495	5.33	1.30	1.65×10^{-3}
0.29	3.95	0.313	13.6	1.33	2.09×10^{-3}

[a] SO_2, SO_3, and O_2 are not in chemical equilibrium with each other. Temperature 450°C.

$$\frac{K(1-\bar{\alpha})/\bar{\alpha}}{\{1+[K(1-\bar{\alpha})/\bar{\alpha}]^{1/2}\}^2}$$

This function gives the reaction rate after correction for the retarding effect of SO_3 [compare formula (4)].

The figure also shows the reaction temperature, the average degree of conversion $\bar{\alpha}$, and the values of n from the relation $v = kp_{O_2}^n$ relating to each line. It was found that below 20% O_2 n approximately equals unity; over 20% O_2 n is much lower, i.e., 0.3–0.4. As shown in Table 1, $n = 1$ is in good agreement with the results obtained by most investigators. The cause of the deviation at higher oxygen concentrations is not clear, however. It is worthwhile stating here that Eklund also found n to deviate from unity above 20% O_2, albeit that he reports a value of ~2.

2. Rate of Reaction as a Function of p_{SO_2} *without* SO_3 *in the Initial Gas*

At $p_{SO_3} \ll p_{SO_2}$, Eq. (4) will change into $v_{SO_3} = kp_{O_2}$. In SO_3-free gas the reaction will therefore be zero order with respect to SO_2. Since the SO_3 formed may, of course, reduce the reaction rate, a correction is made for this effect by means of the term w given above. The catalytic activity is expressed in terms of the reaction rate constant k, i.e., the constant that is first order with respect to oxygen under conditions where no SO_3 is present,

$$k = \frac{v_{SO_3}}{(\text{term } w)p_{O_2}}$$

Table 4 shows that the influence of p_{SO_2} on v_{SO_3} is small (provided p_{O_2} has not been changed) and that that on k is not noticeable. This is in agreement with the experiments by Boreskov, Ritter, and Volkova (*5*) referred to above (see Fig. 1).

3. The Influence of SO_3 *on the Reaction Rate*

In order to perform a check on the validity of kinetic formula (4) the results of the differential measurements on Catalysts

TABLE 4

Influence of p_{SO_2} on the Initial Reaction Rate

Catalyst	Temperature (°C)	p_{O_2} (atm)	$(p_{SO_2})_0$ (atm)	α	v_{SO_3} (g mole/sec g)	w	k (g mole/sec g at.)
3	395°	0.187	0.084	0.090	2.08×10^{-6}	0.51	2.19×10^{-5}
	395°	0.197	0.040	0.154	1.68×10^{-6}	0.42	2.02×10^{-5}
3	454°	0.187	0.087	0.062	1.49×10^{-5}	0.745	1.07×10^{-4}
	455°	0.183	0.087	0.169	1.17×10^{-5}	0.61	1.05×10^{-4}
	456°	0 046	0.042	0.125	3.15×10^{-6}	0.65	1.05×10^{-4}
2	446°	0.187	0.082	0.090	2.42×10^{-6}	0.82	1.58×10^{-5}
	446°	0.195	0.041	0.187	2.51×10^{-6}	0.75	1.71×10^{-5}
	446°	0.200	0.022	0.390	2.78×10^{-6}	0.65	2.14×10^{-5}

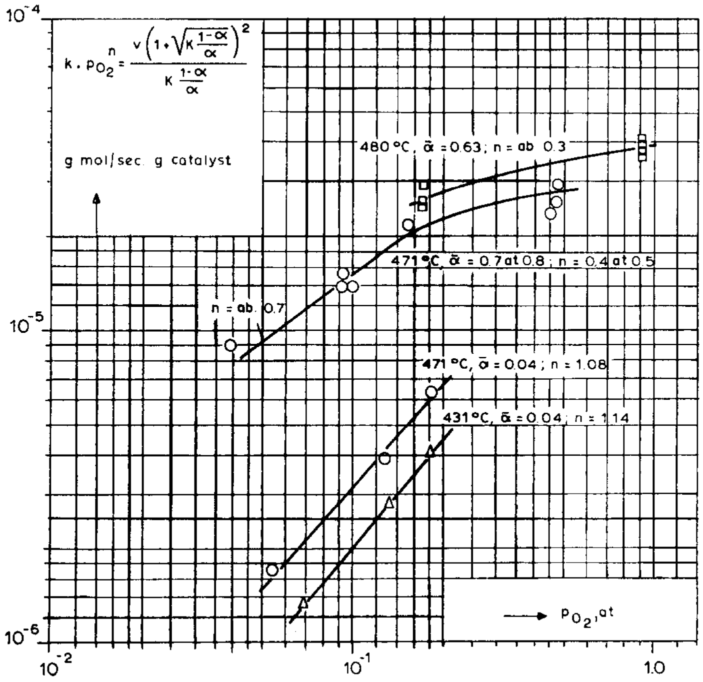

FIG. 4. Reaction rate as function of the partial oxygen pressure. Catalyst; p_{SO_2} ahead of the reactor, 0.06–0.10 atm.

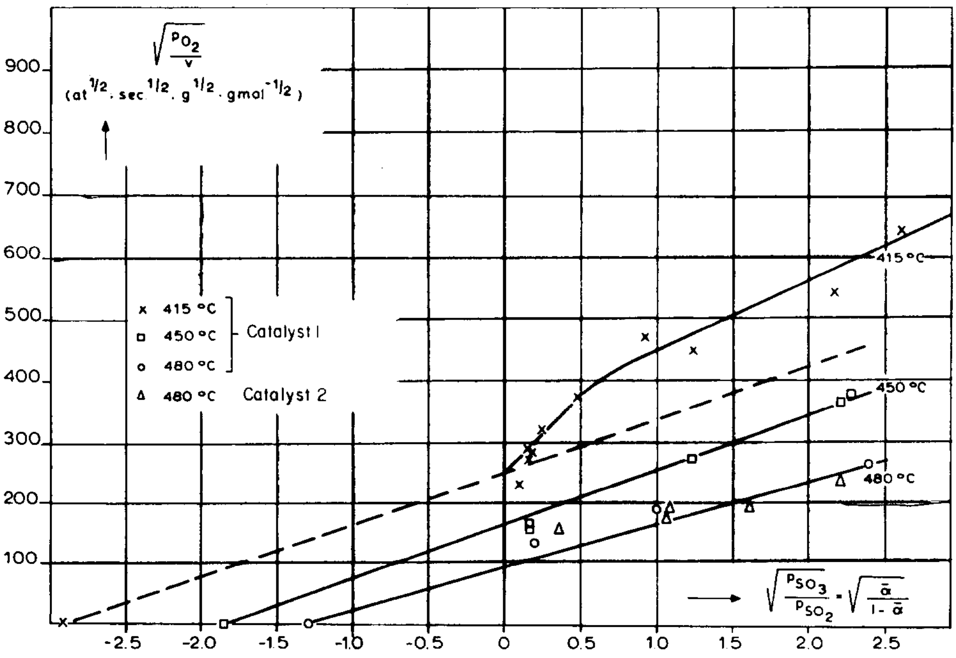

FIG. 5. Results of kinetic measurements on Catalysts 1 and 2 plotted according to Eq. (9). Differential measurements were performed at various levels of conversion formed by variation of the preconversion; $p_{O_2} \simeq 0.19$ atm.

1 and 2 have been plotted (Fig. 5) in conformity with the linearized formula

$$\left(\frac{p_{O_2}}{v}\right)^{1/2} = \left(\frac{1}{k}\right)^{1/2} + \left(\frac{1}{Kk}\right)^{1/2}\left(\frac{p_{SO_3}}{p_{SO_2}}\right)^{1/2} \qquad (9)$$

The partial pressures before and after the catalyst have been averaged.* Figure 5 shows that the measurements at higher temperatures (450°C and upwards) are indeed described by his formula. The values for k and K can be calculated from this figure.

The question arises whether the K values derived from such kinetic data are in conformity with those calculated, by means of (5b), from chemical analyses of $[V^{4+}]/[V^{5+}]$ in the catalyst and p_{SO_2}/p_{SO_3} in the gas phase [see ref. (*13*)]; the latter will further be denoted as K_{anal}. It appears quite feasible to draw a line through the experimental points, starting from $[-(K_{anal})^{1/2}, 0]$. This shows that the agreement is satisfactory between the mechanism and the derived kinetics of this process. At temperatures below 450°C, however, there appears to be a distinct deviation from the proposed kinetic formula.

The results of the measurements performed on Catalyst 3 have been plotted in the same way (see Fig. 6). The equilibrium position (5b) for this catalyst with its high sodium content not being known as a function of temperature, it was determined by analysis of the V^{4+}/V^{5+} ratio in the catalyst and of the SO_2/SO_3 ratio in the gas phase. The straight line drawn through the experimental points lies under that of Catalyst 1 (Fig. 7).

From the results obtained from the kinetic measurements on Catalyst 3 (see Fig. 6)* it appears that the kinetic views suggested above are also applicable to this catalyst under high-temperature conditions (above 420°C). Further, the values found prove to lie on a straight line, which intersects the axis in a point $[-(K_{anal})^{1/2}, 0]$ determined by the analytically determined value of K. Hence, the formula (4) indeed describes the rate of the SO_3 formation at elevated temperatures. A deviating trend is again noted upon a decrease in temperature. Now that the basic pattern of the

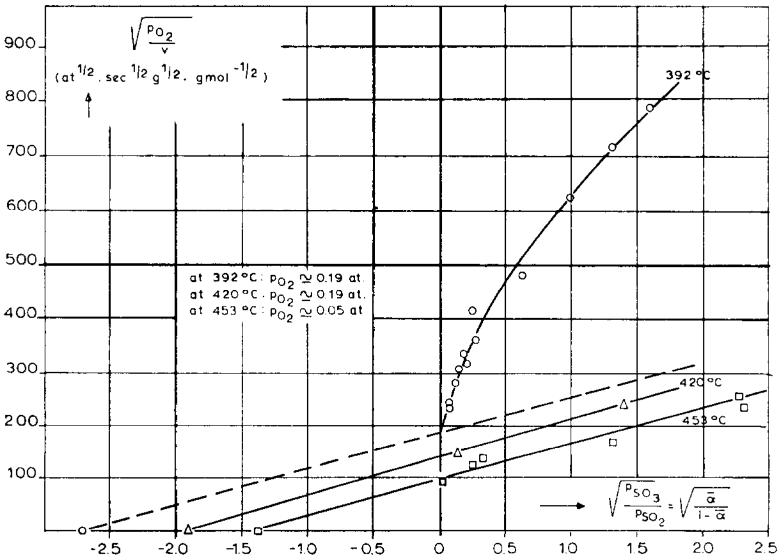

FIG. 6. Results of kinetic measurements on Catalyst 3 according to Eq. (9). Differential measurements were performed at various levels of conversion formed by variation of the preconversion.

---

* The reverse reaction has been neglected here. At high degrees of conversion the value of the ordinate may be at most 7% too high.

* The reverse reaction has been neglected here. At high degrees of conversion the value of the ordinate may be at most 7% too high.

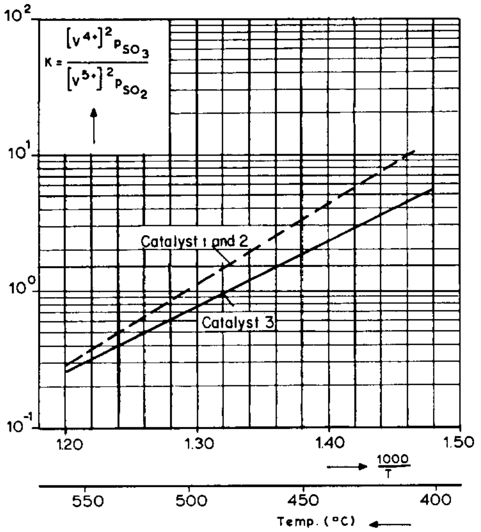

FIG. 7. Values of the equilibrium constant $K = [V^{4+}]^2 p_{SO_3}/[V^{5+}]^2 p_{SO_2}$ on the two types of catalyst as a function of the temperature.

kinetics has been established, some further points remain to be discussed: (a) the deviating trend at lower temperatures; (b) *k* as a function of the temperature. Is there a break in the Arrhenius curve?

a. The deviation from normal kinetic behavior at lower temperatures. (See Figs. 5 and 6.) From the sequence of the experiments it can be concluded that this effect is not caused by insufficient establishing of stationary conditions. This phenomenon may be formulated as follows: At low temperatures the rate-retarding effect of SO_3 is stronger than would follow from formula (2). This effect is stronger in Catalyst 3 than in Catalyst 1. It cannot be due to the formation of polysulfate ions $(S_3O_{10})^{2-}$ (see the ratio S/(Na + K) in Fig. 4), but, perhaps, it is to be sought in the formation of sulfovanadates. Such sulfo groups might enclose and stabilize the V^{4+}. Another possibility is that at lower temperatures the desorption of SO_3 influences the reaction rate.

Our experimental information does not enable us to decide which of these possible causes has the strongest effect.

b. *k* as function of the temperature. Does the Arrhenius curve contain a break? If the influence of SO_3 on the forward reaction can be quantitatively described in the way outlined above, the value of the

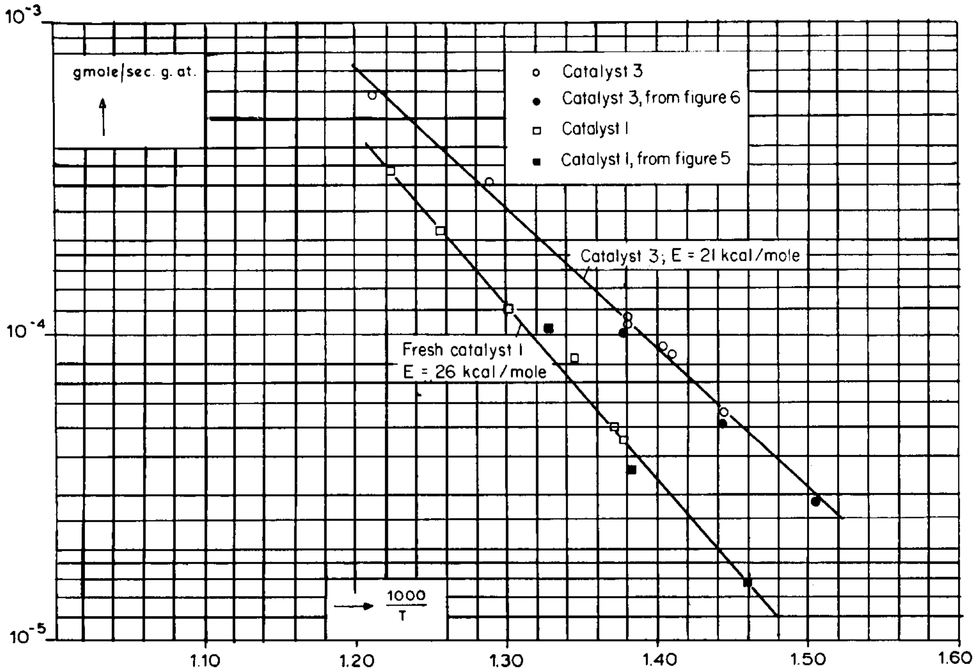

FIG. 8. Calculated rate constant as function of the temperature (measurements on small catalyst grains: 0.5–0.7 mm).

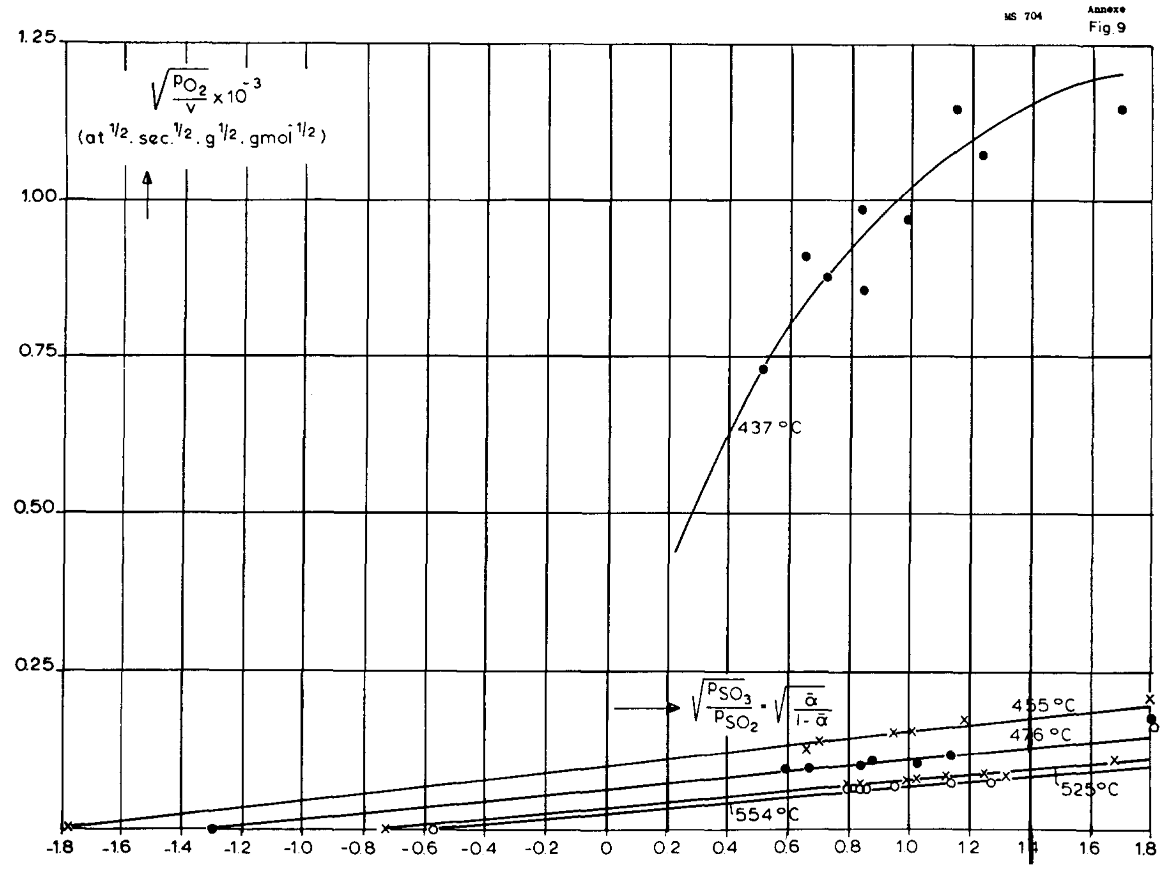

FIG. 9. Results of Eklund's measurements (*7*), represented according to Eq. (9).

reaction rate constant k can be calculated as a function of the temperature. If the theory is correct, the Arrhenius plot will not develop a break as is generally observed upon application of other reaction rate constants (*13, 17*). Included in Fig. 8 are the k values found by extrapolating the experimental results illustrated in Figs. 5 and 6 towards $\alpha = 0$, and also those calculated from the results of some individual experiments at other temperatures by means of Eq. (4). This figure shows that application of the derived kinetics does not produce a break in the Arrhenius curve.

4. Comparison with the Literature

The kinetics examined in this study represent the slowdown caused by SO_3 somewhat differently than other formulas. At very low K values our formula (4) changes into the Boreskov formula (1), wherein $n = 1$. Then, the lines through the experimental points in Figs. 5 and 6 are not drawn through $(-K^{1/2}, 0)$ but through the origin.

In Fig. 9 Eklund's experimental results have been plotted in the same way as in Figs. 5 and 6, and the lines have been drawn through the $[-(K_{\text{anal}})^{1/2}, 0]$ values corresponding to the various temperatures. The points relating to temperatures of 455°C, and above, nearly all give a very close fit and Eklund quite understandably states that his reaction rate constant (see Table 1) varies systematically with the degree of SO_2 conversion. Consequently, Eq. (4) is, in fact, more appropriate than his own. It is remarkable that Eklund's results obtained at lower temperatures (437°C) also deviate from those found at higher temperatures, in the same way as was noted by us.

The new formula of Boreskov *et al.* (*12*),

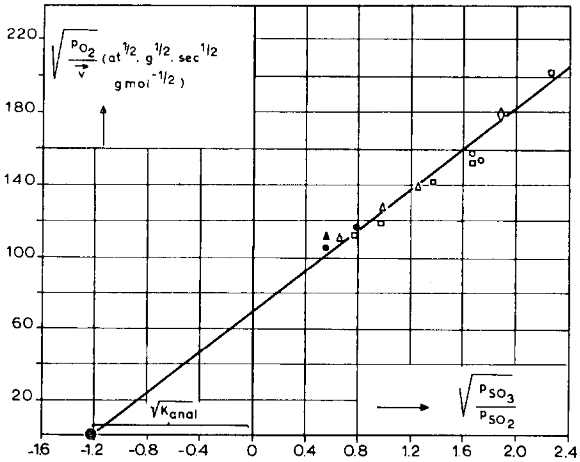

FIG. 10. Results of experiments of Boreskov *et al.* (*12*), represented according to Eq. (9).

i.e., (2), resembles very much our formula (4). In Fig. 10 the experimental results which form the basis for (2) are plotted according to the linearized form of formula (4). This figure shows that also these results are in accordance with our kinetic expression; moreover, the value of the constant K is identical with that derived from analytical determination.

REFERENCES

1. Boreskov, G. K., and Pligunov, V. P., *J. Appl. Chem. USSR* (*Zh. Priklad. Khim.*) **6**, 785 (1933).

2. Boreskov, G. K., *Chem. Abstr.* **29**, 6371 (1935).

3. Boreskov, G. K., and Sokolova, F. J., *J. Chem. Ind. USSR* **14**, 1241 (1937).

4. Brodovich, K. J., *J. Appl. Chem. USSR* **14**, 894 (1941); *Chem. Abstr.* **39**, 3997 (1945).

5. Boreskov, G. K., Ritter, L. G., and Volkova, E. J., *Chem. Abstr.* **43**, 8251 (1949); *J. Appl. Chem. USSR* **22**, 250 (1949).

6. Calderbank, P. H., *J. Appl. Chem.* (*London*) **2**, 482 (1952).

7. Eklund, R.-B., "The Rate of Oxidation of Sulphur Dioxide with a Commercial Vanadium Catalyst." Thesis, Stockholm, 1956.

8. Goldman, M., Canjar, L. N., and Beckmann, R. B., *J. Appl. Chem.* (*London*) **7**, 275 (1957).

9. Zakarevski, M. S., and Chang, Man-Cheng, *Chem. Abstr.* **53**, 13755 (1959); Chang, Man-Cheng c.s., *Chem. Abstr.* **57**, 16127 (1962).

10. Rzaev, P. B., Roiter, V. A., and Korneichuk, G. P., *Ukr. Khim. Zh.* **26**, 161 (1960).

11. Davidson, B., and Todes, G., *A.I.Ch.E. J.* **10**, 568 (1964).

12. Boreskov, G. K., Buyanov, R. A., and Ivanov, A. A., *Kinetika i Kataliz* **8**, 153 (1967).

13. Mars, P., and Maessen, J. G. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 266.

14. Fraser, J. H., and Kirkpatrick, W. J., *J. Am. Chem. Soc.* **62**, 1659 (1940).

15. Topsøe, H. F. A., and Nielsen, A., Trans. Danish Acad. of Technical Sciences, No. 1, p. 3 (1948).

16. Tandy, G. H., *J. Appl. Chem.* (*London*) **6**, 68 (1956).

17. Gerburt-Geibowitsch, E. V., and Boreskov, G. K., *J. Phys. Chem. USSR* **30**, 1801 (1956).