our choice of relative pressure. For P/P_0 used in these studies cross checks reveal that hysteresis effects are trivial.

This method may be usable for measurements of pores in other ranges of diameters by varying the composition of the N_2:He stream, i.e., P/P_0. Checks should be made, however, to assure that the adsorption–desorption occurring during pressurization at such relative pressures does not introduce hysteresis effects which can spoil agreement with traditional evaluation methods.

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REFERENCES

1. HOLMES, J., AND EMMETT, P. H., *J. Phys. Colloid. Chem.* **51**, 1262 (1951).
2. HALEY, A. J., Presented: Meet. *AIChE, 52nd,* Feb. 5, 1964.
3. HALEY, A., *J. Appl. Chem.* **13**, 392 (1963).
4. INNES, W. B., *Anal. Chem.* **23**, 759 (1951).
5. BARRETT, E. P., JOYNER, L. G., AND HALENDA, J. P., *J. Amer. Chem. Soc.* **73**, 373 (1951).
6. BALLOU, E. V., AND DOOLEN, O. K., *Anal. Chem.* **32**, 533 (1960).
7. BRUNAUER, S., EMMETT, P. H., AND TELLER, E., *J. Amer. Chem. Soc.* **60**, 309 (1938).

EDWIN W. LARD
STANLEY M. BROWN

W. R. Grace & Co., Research Division
Clarksville, Maryland 21029
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Remarks on the Reduction–Oxidation Mechanism of Sulfur Dioxide Oxidation on Vanadium Catalyst

NOMENCLATURE

A_1	frequency factor [g-mole/(hr)(atm)(g catalyst)]
A_2	parameter in Eq. (12)
E_1	activation energy (cal/g-mole)
E_2	parameter in Eq. (12)(cal/g-mole)
k	rate constant [g-mole/(hr)(atm)(g catalyst)]
K	equilibrium constant defined as $K = c_{V^{4+}}^2 p_{SO_3}/c_{V^{5+}}^2 p_{SO_2}$
$c_{V^{4+}}$, $c_{V^{5+}}$	concentration of vanadium in oxidation state +4 or +5
K_p	equilibrium constant of sulfur dioxide oxidation defined by partial pressures ($\text{atm}^{-1/2}$)
p_i	partial pressures of species i (atm)
r_0	initial reaction rate [g-mole/(hr)(g catalyst)]
r	reaction rate [g-mole/(hr)(g catalyst)]
$\hat{r}$	calculated reaction rate [g-mole/(hr)(g catalyst)]
R	gas constant [cal(mole)(°K)]
T	absolute temperature (°K)

I. INTRODUCTION

In 1964 Mars and Maessen (*1*) proposed an reduction–oxidation mechanism for the catalytic oxidation of sulfur dioxide on potassium–vanadium oxide catalyst. Since that time, this mechanism has been the subject of many studies (*2–5*). Mars and Maessen (*1*) assumed that the catalytic oxidation of sulfur dioxide proceeds via the following reaction steps:

$$SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}, \qquad (1)$$

$$\tfrac{1}{2} O_2 + 2V^{4+} \rightleftarrows 2V^{5+} + O^{2-}. \qquad (2)$$

They further assumed that the surface reaction described by Eq. (1) is fast compared to the reduction–oxidation reaction of Eq. (2), and that the reduction–oxidation reaction is rate controlling. In continuation of this original work Mars and Maessen (*2*) studied the oxidation reaction on a sodium–potassium–vanadium catalyst and found that the reaction rate can also be described by the above mechanism.

As shown by Regner and Šimeček (*3*), the reduction–oxidation reaction step may be decomposed to several substeps. Various rate expressions can readily be developed assuming that one of these subsets is rate determining. These expressions are summarized and discussed elsewhere (*3–5*). Table 1 lists the rate expressions which are abstracted from the work of Regner and Šimeček (*3*). In these expressions K_p is the thermodynamic equilibrium constant for the reaction

$$SO_2 + \tfrac{1}{2}\,O_2 = SO_3.$$

An interesting feature of the rate expressions, as shown in Table 1, would be that all the reaction mechanisms lead to the strikingly similar hyperbolic models. Because of this fact screening and discrimination of these models are, in general, quite troublesome. A procedure which has been frequently employed in kinetic studies is to discriminate among plausible rate models in the light of the values of the standard deviation of the residuals and the signs of estimated parameters. The procedure, however, is not highly recommended for general use. This is particularly true for the case where a number of hyperbolic models are postulated and kinetic data were gathered in a random manner. As indicated by Lapidus and Peterson (*6*), such hyperbolic models often yield virtually the same standard deviations. For the use of estimated parameters in the selection of suitable models, there are a number of factors which must be examined. They involve the joint confidence region of converged parameter estimates, the goodness of fits, and the nature of the sum of squares surfaces. It thus appears that the sole use of the standard deviation and parameter estimates, in many cases, will yield no conclusive results in distinguishing many rival hyperbolic models. This constitutes no exception to the catalytic oxidation of sulfur dioxide.

The main purpose of this communication is to present that consideration of initial rate data is quite effective for the elimination of Mars–Maessen-type models which are obviously inadequate in describing the catalytic oxidation rate of sulfur dioxide. In this work it was also attempted to select the best Mars–Maessen rate model through the conventional statistical techniques.

II. The Reduction–Oxidation Rate Models

As described previously the reaction scheme of the Mars–Maessen reaction model can be expressed by Eqs. (1) and (2). Eq. (3) of Table 1 is derived by assuming that the adsorption of oxygen, namely, the second step, is rate controlling. Mars and Maessen determined the values of the adsorption equilibrium constant K from their equilibrium studies (*1, 2*) and found that for the potassium–vanadium catalyst K is given by the following relationship:

$$K = 2.3 \times 10^{-8} \exp(27200/RT). \tag{9}$$

For the sodium–potassium–vanadium catalyst Šimeček (*5*) calculated the value of K using the data of Mars and Maessen and obtained

$$K = 7.06 \times 10^{-7} \exp(21200/RT). \tag{10}$$

On the basis of Mars–Maessen's reaction scheme Regner and Šimeček (*3*) considered more elaborated steps for the adsorption of oxygen and developed five plausible models. In Table 1 these models are summarized along with proposed rate-determining step. Note that step (6) may not be a mechanistic step. But we derived the rate expression of (3), treating the step as a mechanistic step. Regner and Šimeček employed the values of the mean relative deviations of constant k and selected the rate Eq. (7) as most appropriate for the presentation of their oxidation data (*9*). More recently Šimeček and co-workers (*4*) verified the suitability of the rate Eq. (4) using kinetic data which were gathered on two types of commercial vanadium catalyst: one contains potassium and the other contains sodium and potassium as active components.

The summary of results of these previous investigations would indicate that almost all Mars–Maessen-type rate expressions yield the similar fits to experimental rate

TABLE 1

REACTION MECHANISMS FOR SULFUR DIOXIDE OXIDATION

Mechanism	Reaction steps	Controlling step	Rate expression	Eq. no.
I	(a) $SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}$			
	(b) $\frac{1}{2} O_2 + 2V^{4+} \rightleftarrows 2V^{5+} + O^{2-}$	(b)	$r = \frac{kKp_{SO_2}p_{O_2}^{1/2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}]^2} \Big\} 1 - \frac{p_{SO_3}}{K_p p_{SO_2} p_{O_2}^{1/2}} \Big\{$	(3)
II	(c) $SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}$			
	(d) $O_2 + 2V^{4+} \rightleftarrows 2V^{5+} + 2O^-$	(d)	$r = \frac{kKp_{SO_2}p_{O_2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}]^2} \Big\} 1 - \frac{p_{SO_3}^2}{K_p^2 p_{SO_2}^2 p_{O_2}} \Big\{$	(4)
III	(e) $O^- + V^{4+} \rightleftarrows V^{5+} + O^{2-}$	(e)	$r = \frac{kKp_{SO_2}p_{O_2}^{1/2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}](p_{SO_3})^{1/2}} \Big\} 1 - \frac{p_{SO}}{K_p p_{SO_2} (p_{O_2})^{1/2}} \Big\{$	(5)
	(f) $SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+}$			
	(g) $O_2 + V^{4+} \rightleftarrows V^{5+} + O_2^-$	(g)	$r = \frac{k(Kp_{SO_2})^{1/2}p_{O_2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}]} \Big\} 1 - \frac{p_{SO_3}^2}{K_p^2 p_{SO_2}^2 p_{O_2}} \Big\{$	(6)
	(h) $O_2^- + V^{4+} \rightleftarrows V^{5+} + 2O^-$	(h)	$r = \frac{kKp_{SO_2}p_{O_2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}](p_{SO_3})^{1/2}} \Big\} 1 - \frac{p^2{}_{SO_3}}{Kp^2 p_{SO_2}^2 p_{O_2}} \Big\{$	(7)
	(i) $O^- + V^{4+} \rightleftarrows V^{5+} + O^{2-}$	(i)	$r = \frac{kKp_{SO_2}(p_{O_2})^{1/2}}{[(p_{SO_3})^{1/2} + (Kp_{SO_2})^{1/2}](p_{SO_3})^{1/2}} \Big\} 1 - \frac{p_{SO_3}}{K_p p_{SO_2} (p_{O_2})^{1/2}} \Big\{$	(8)

data and that the sole use of goodness-of-fit provide little knowledge concerning the distinct superiority of one model over the other. This result can be foreseeable in the light of articles which relate to the characteristics of hyperbolic rate models (*6, 10, 11*).

It appears, however, that the use of initial oxidation rates is of great help to eliminate certain models incapable of describing the reaction. Moreover, this elimination of grossly inadequate models definitely simplifies the specification of the remaining rate models. Table 2 shows the initial rate expressions of rate equations of Table 1. These expressions were obtained purely mathematically with the assumption that the feed does not contain SO_3. As pointed out by Mars and Maessen (*2*), sulfur trioxide gas has a profound influence on reducing the oxidation rate. Under the extreme experimental conditions wherein no sulfur trioxide is present, the oxidation rate may actually be quite fast, but the rate must be finite. In cases where the initial rates are controlled by diffusion process of the reactants or the product, the rates should approach these diffusion rates. On this ground the rate models (5), (7), and (8) are not adequate. All the remaining models, that is, (3), (4), and (6) provide the initial oxidation rates which are proportional to the partial pressure of oxygen and/or its square root, respectively. If the rate data is taken for experimental conditions in which the partial pressures of oxygen is varied keeping the partial pressure of sulfur dioxide constant, then an adequacy test of these three models can readily be performed.

TABLE 2
INITIAL REACTION RATES FOR SULFUR DIOXIDE OXIDATION

Eq. no.	Initial reaction rates
(3)	$r_0 = kp_{O_2}^{1/2}$
(4)	$r_0 = kp_{O_2}$
(5)	$r_0 \to \infty$
(6)	$r_0 = kp_{O_2}$
(7)	$r_0 \to \infty$
(8)	$r_0 \to \infty$

III. NONLINEAR ESTIMATION OF RATE PARAMETERS

The temperature-dependent models were developed by introducing an Arrhenius type relationship for the constants k and K. The relationships employed here were

$$k = A_1 e^{-E_1/RT} \tag{11}$$

and

$$K = A_2 e^{E_2/RT}. \tag{12}$$

The Arrhenius parameters of rate expression (3), (4), or (6) were estimated by a nonlinear least squares technique. The rate parameters are four in number; they are A_1, A_2, E_1, and E_2. The thermodynamic equilibrium constant K_p was computed by a relationship given by Boreskov (*12*). For the estimation we used two different sets of rate data: one is a group of data gathered by Kadlec and Pour (*7*). The SVD catalyst was utilized for this investigation. The catalyst contained potassium as the active component. The detailed data concerning the catalyst is given elsewhere (*7*). The reaction temperatures ranged from 460 to 520°C and the gas compositions of feed were 7 and 10% SO_2 with 11% O_2. The second set of data is that reported by Kadlec and co-workers (*8*). The catalyst utilized was a ICI catalyst containing both sodium and potassium as active components. We obtained the estimates of rate parameters using only the data taken at 380–480°C. At temperatures higher than 480°C, Kadlec and co-workers (*8*) found that the effect of internal diffusion on the oxidation rate is not negligible. For this reason, the data collected at 500 and 520°C were discarded for our study. The composition of feed was 10% of SO_2 and 11% of O_2.

The objective function (*13*) was minimized with respect to four parameters (A_1, A_2, E_1, and E_2) to obtain the best estimates of parameters.

$$\sum_{i=1}^{N} \left(\frac{r_i - \hat{r}_i}{r_i}\right)^2. \tag{13}$$

TABLE 3

PARAMETER ESTIMATES FOR RATE EQUATIONS

Rate Eq.	Catalyst	Parameter estimates				Sum of squares of residual rates	Mean square
		A_1	E_1	A_2	E_2		
3	SVD	1.04×10^{16}	5.47×10^{4}	2.86×10^{-9}	2.42×10^{4}	1.97×10^{-3}	3.79×10^{-5}
4	SVD	5.11×10^{14}	4.92×10^{4}	5.07×10^{-9}	2.70×10^{4}	2.56×10^{-3}	4.93×10^{-5}
6	SVD	2.14×10^{15}	4.76×10^{4}	1.26×10^{-12}	2.71×10^{4}	4.07×10^{-3}	7.83×10^{-5}
3	ICI	1.17×10^{16}	5.24×10^{4}	2.56×10^{-9}	2.32×10^{4}	3.59×10^{-4}	8.15×10^{-6}
4	ICI	7.34×10^{14}	4.72×10^{4}	1.17×10^{-9}	2.73×10^{4}	1.69×10^{-4}	3.84×10^{-6}
6	ICI	6.83×10^{15}	4.62×10^{4}	3.07×10^{-14}	2.90×10^{4}	1.20×10^{-3}	2.73×10^{-5}

The resulting best estimates of parameters in Eqs. (3), (4), and (6) are shown in Table 3.

The adequacy of rate models of Eqs. (3), (4), and (6) was examined by two methods: examination of residual rates and the analysis of variance. The residual rates obtained from these rate expressions are randomly distributed and showed no systematic pattern with any of the dependent and independent variables. However, all the models examined here exhibited relatively large random values of residuals for the data taken at 380°C with the ICI catalyst. This suggests that the models may not be entirely satisfactory in correlating low temperature rates or that large experimental errors may be involved with low reaction rates. The results of the analysis of variance are presented in Table 4. The results

TABLE 4

THE ANALYSIS OF VARIANCE

Catalyst:	SVD			ICI		
Rate Eq.:	3	4	6	3	4	6
Residual						
Sum of squares	1.97×10^{-3}	2.56×10^{-3}	4.07×10^{-3}	3.59×10^{-4}	1.69×10^{-4}	1.20×10^{-3}
Degree of freedom	52	52	52	44	44	44
Experimental error						
Sum of squares	2.18×10^{-4}	2.18×10^{-4}	2.18×10^{-4}	2.55×10^{-5}	2.55×10^{-5}	2.55×10^{-5}
Degree of freedom	5	5	5	11	11	11
Mean square	4.36×10^{-5}	4.36×10^{-5}	4.36×10^{-5}	2.32×10^{-6}	2.32×10^{-6}	2.32×10^{-6}
Lack of fit						
Sum of squares	9.75×10^{-3}	2.34×10^{-3}	2.85×10^{-3}	3.33×10^{-4}	1.43×10^{-4}	1.17×10^{-3}
Degree of freedom	47	47	47	33	33	33
Mean square	2.08×10^{-4}	4.98×10^{-5}	8.21×10^{-5}	1.01×10^{-5}	4.33×10^{-6}	3.55×10^{-5}
Variance ratio	4.77	1.14	1.88	4.35	1.87	15.30
5% F-statistic	4.44	4.44	4.44	2.57	2.57	2.57
Model adequacy	No	Yes	Yes	No	Yes	No

indicate that the rate expression (3) is not adequate for the system considered, and that the reaction models (4) and (6) are equally acceptable for the presentation of the data set gathered with the SVD catalyst; whereas model (6) is not suitable for the data taken with the ICI catalyst.

With regard to the parameter estimates, the agreement between E_2 of models (4) and (6) and the orginally reported value 27,200 cal/g-mole should be noted. For these cases, however, the estimates of pre-exponential factor, A_2 do not agree with that of Mars and Maessen. Also note from Table 3 that a consistency in the magnitudes of A_1, E_1, and E_2 exists for the two catalysts and a given rate equation. The estimates of A_2, however, did not agree, especially for Eq. (6). It may imply that Eq. (6) is not suitable for the description of the data employed.

IV. CONCLUSIONS

Mars–Maessen-type rate models were examined for their adequacies by using existing rate data which were collected with the two different vanadium oxide catalysts. The use of initial reaction rates appears to provide definitive conclusions regarding the discrimination of the rate models. The model given by Eq. (4) is found adequate for the oxidation reaction inside of the following experimental conditions: the reaction temperature 380–520°C and the gas compositions of feed $7 \sim 10\%$ SO_2 and 11% O_2. For the outside region of these experimental conditions more experimental data are needed to discuss the adequacy of the model (4).

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REFERENCES

1. MARS, P., AND MAESSEN, J. G. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam,* 1964, North-Holland, Amsterdam, Vol. 1, p. 266 (1965).
2. MARS, P., AND MAESSEN, J. G. H., *J. Catal.* **10,** 1 (1968).
3. REGNER, A., AND ŠIMEČEK, A., *Collect. Czech. Chem. Commun.* **33,** 2540 (1968).
4. ŠIMEČEK, A., KADLEC, B., AND MICHALEK, J., *J. Catal.* **14,** 287 (1969).
5. ŠIMEČEK, A., *J. Catal.* **18,** 83 (1970).
6. LAPIDUS, L., AND PETERSON, T. I., *AIChE J.* **11,** 891 (1965).
7. KADLEC, B., AND POUR, V., *Collect. Czech. Chem. Commun.* **33,** 2526 (1968).
8. KADLEC, B., MICHÁLEK, J., AND ŠIMEČEK, A., *Chem. Eng. Sci.* **25,** 319 (1970).
9. ŠIMEČEK, A., REGNER, A., AND VOSOLSOBĚ, J., *Collect. Czech. Chem. Commun.* **33,** 2162 (1968).
10. BOX, G. E. P., AND LUCAS, H. L., *Biometrika* **46,** 77 (1959).
11. MEZAKI, R., AND KITTRELL, J. R., *AIChE J.* **14,** 513 (1968).
12. BORESKOV, G. K., *in* "The Catalysis in Sulfuric Acid Industry," p. 16. Moscow, 1954.

R. MEZAKI

Chemical Engineering Department
New York University
University Heights, Bronx, New York 10453

B. KADLEC

Department of Inorganic Technology
Technical University
Prague 6, Czechoslovakia

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