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A Theoretical Model Suitable for Higher Conversion Data of Sulfur Dioxide Oxidation

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A theoretical model has been developed to adequately correlate higher conversion data of sulfur dioxide oxidation. The model includes a potential term with an apparent stoichiometric number which is, in general, a function of experimental conditions. The usefulness of the model is demonstrated by employing existing kinetic data for the oxidation reaction.

NOMENCLATURE

A_1	Frequency factor [g-mole/(hr)(atm)(g-catalyst)]
A_2	Parameter in Eq. (19)
E_1	Activation energy (cal/g-mole)
E_2	Parameter in Eq. (19)
k	Rate constant [g-mole/(hr)(atm)(g-catalyst)]
K	Rate constant
K_p	Thermodynamic equilibrium constant of sulfur dioxide oxidation (atm^{-1})
N	Number of observations
p_i	Partial pressure of species i (atm)
r_i	Observed reaction rate of i-th experiment [g-mole/(hr)(g-catalyst)]
$\hat{r}_i$	Calculated reaction rate of i-th experiment [g-mole/(hr)(g-catalyst)]
R	Gas constant [cal/(g-mole)(°K)]
T	Absolute reaction temperature (°K)
v_{+i}	Forward reaction rate of elementary step i [g-mole/(hr)(g-catalyst)]
v_{-i}	Backward reaction rate of elementary step i [g-mole/(hr)(g-catalyst)]
V	Overall reaction rate [g-mole/(hr)(g-catalyst)]
$V_+^{(p)}$	Unidirectional overall forward reaction rate for the path p [g-mole/(hr)(g-catalyst)]
$V_-^{(p)}$	Unidirectional overall backward reaction rate for the path p [g-mole/(hr)(g-catalyst)]
ΔG	Gibbs free energy change (cal/g-mole)
ν	Stoichiometric number
$\bar{\nu}$	Apparent stoichiometric number
$\bar{\nu}_{S\text{-}35}$	Apparent stoichiometric number determined with sulfur-35
φ	Objective function

I. INTRODUCTION

The catalytic oxidation of sulfur dioxide has been the subject of extensive research with regard to determination of reaction mechanism and kinetic modeling. This is because the reaction has been widely used for manufacturing sulfuric acid and because sulfur dioxide and its oxidation products are important atmospheric pollutants. A review by Weychert and Urbanek (*1*) summarizes numerous rate expressions which have been postulated for the oxidation reaction. Many of these expressions are not entirely satisfactory to describe the oxidation rate of sulfur dioxide over a wide range of experimental conditions. For example, rate expressions which exclude terms related to the partial pressure of sulfur trioxide cannot correlate the data taken at conditions close to equilibrium of sulfur dioxide oxidation.

Recently some attention has been directed toward modeling near chemical equilibrium (*2*). In connection with atmospheric pollution caused by sulfur dioxide it was felt important that a rate expression which can adequately describe the oxidation data gathered in the vicinity of equilibrium be developed. The attainment of the equilibrium conversion of the oxidation system may be particularly attractive for the manufacturers of sulfuric acid. This would not only improve the efficiency of sulfur utilization, but also minimize the capital expenditure for the treatment of tail gas.

It was attempted in the present study to develop a novel theoretical rate expression which ensures success in correlating rate data of high conversion. In addition the usefulness of the expression was demonstrated by using existing kinetic data for the oxidation reaction.

II. DEVELOPMENT OF RATE MODEL

For the oxidation of sulfur dioxide,

$$2SO_2 + O_2, = 2SO_3 \qquad (1)$$

we now assume that the reaction comprises the following elementary steps:

Step no.	Elementary reaction	Stoichiometric no. ν	
1	$O_2 + 2(l) \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} 2O(l)$	1	
2	$SO_2 + (l) \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} SO_2(l)$	2	
3	$SO_2(l) + O(l) \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} SO_3(l) + (l)$	2	(2)
4	$SO_3(l) \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} SO_3 + (l)$	2	

The stoichiometric number ν is defined as the number of times each elementary step occurs for a single occurrence of the overall reaction.

Recently Csuha and Happel (*3*) obtained a generalized relationship between the Gibbs free energy change and the forward and backward rate of each elementary step. Applying this relationship to our system, we obtain

$$\exp(-\Delta G/RT) = \frac{v_{+1}}{v_{-1}}\left[\frac{v_{+2}v_{+3}v_{+4}}{v_{-2}v_{-3}v_{-4}}\right]^2. \qquad (3)$$

Our recent study (*4*) with oxygen-18 indicated that step 2 and step 3 are at equilibrium and that the adsorption of oxygen (step 1) and the desorption of sulfur trioxide (step 4) may be rate-controlling. Thus we obtain the following relationship:

$$\frac{v_{+2}}{v_{-2}} \cong \frac{v_{+3}}{v_{-3}} \cong 1. \qquad (4)$$

Substituting Eq. (4) into Eq. (3), we obtain

$$\exp(-\Delta G/RT) = \frac{v_{+1}}{v_{-1}}\left[\frac{v_{+4}}{v_{-4}}\right]^2. \qquad (5)$$

It has been widely accepted that the use of isotopic tracers is one of the most powerful techniques in pinpointing rate-controlling step or steps of solid-catalyzed gaseous reaction system. For mechanistic investigation of the catalytic oxidation of sulfur dioxide two kinds of tracers may be employed, oxygen-18 and sulfur-35. When reactant oxygen is tagged with oxygen-18, the isotope is transmitted through the so-called oxygen-path (step 1, step 3, and step 4). If sulfur dioxide gas is marked with sulfur-35, the transfer of this sulfur-35 occurs through the sulfur-path (step 2, step 3, and step 4). The overall oxidation rate can be described as the difference between the forward and backward rates of each path. Hence

$$V = V_+^{1,3,4} - V_-^{1,3,4}, \qquad (6)$$

and

$$V = V_+^{2,3,4} - V_-^{2,3,4}. \qquad (7)$$

In his review article, Happel (*5*) developed the following generalized relationship between the forward and backward rates of a path and the rates of elementary steps involved:

$$\frac{V_+^{(p)}}{V_-^{(p)}} = \frac{v_{+1}v_{+2}\ \cdot\cdot\cdot\ v_{+n}}{v_{-1}v_{-2}\ \cdot\cdot\cdot\ v_{-n}}. \qquad (8)$$

The application of the relationship to our system yields

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \frac{v_{+1}}{v_{-1}} \cdot \frac{v_{+4}}{v_{-4}}, \tag{9}$$

$$\frac{V_+^{2,3,4}}{V_-^{2,3,4}} = \frac{v_{+4}}{v_{-4}}. \tag{10}$$

Note that in derivation of Eqs. (9) and (10) the relation of Eq. (4) is employed.

The ratio of the forward and backward rates of a path can be presented in terms of the apparent stoichiometric number. For the sulfur path we have

$$\bar{\nu}_{S\text{-}35} = \frac{-\Delta G}{RT \ln\left[\dfrac{V_+^{2,3,4}}{V_-^{2,3,4}}\right]}, \tag{11}$$

where $\bar{\nu}_{S\text{-}35}$ is the apparent stoichiometric number obtained using sulfur-35. As can be seen from the subsequent section, $\bar{\nu}_{S\text{-}35}$ is not constant, but is dependent upon experimental conditions. However, $\bar{\nu}_{S\text{-}35}$ may be constant for a narrow region of experimental conditions. Under circumstances wherein $\bar{\nu}_{S\text{-}35}$ varies with experimental conditions, $\bar{\nu}_{S\text{-}35}$ can be described by a function of independent variables such as reaction temperature, and the partial pressures of reactants and products.

From Eqs. (10) and (11) we get

$$\exp\left(-\frac{\Delta G}{\bar{\nu}_{S\text{-}35} RT}\right) = \frac{v_{+4}}{v_{-4}}. \tag{12}$$

Combination of Eqs. (5), (9), and (12) yields

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \exp\left[-\frac{\Delta G}{RT}\left(1 - \frac{1}{\bar{\nu}_{S\,35}}\right)\right]. \tag{13}$$

From Eqs. (6) and (13) we obtain the following expression for the overall oxidation rate of sulfur dioxide.

$$V = V_+^{1,3,4}[1 - (e^{\Delta G/RT})^{[1-(1/\bar{\nu}_{S\text{-}35})]}]. \tag{14}$$

For the catalytic oxidation of sulfur dioxide the Gibbs free energy change, ΔG, is expressed as

$$\Delta G = RT \ln\left[\frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2} K_p}\right]. \tag{15}$$

Hence

$$V = V_+^{1,3,4}\left[1 - \left(\frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2} K_p}\right)^{[1-(1/\bar{\nu}_{S\text{-}35})]}\right], \tag{16}$$

where K_p is the thermodynamic equilibrium constant of the oxidation reaction. Equation (16) conforms to the fact that the net oxidation rate V is approximately equal to $V_+^{1,3,4}$ for experimental conditions removed from equilibrium. A number of techniques are available to construct an adequate model for $V_+^{1,3,4}$. In fact many of the existing models may be directly applicable to represent the overall forward rate of the oxidation reaction.

The value of $\bar{\nu}_{S\text{-}35}$ can change from two to infinity. When the sulfur path is rate-controlling, $\bar{\nu}_{S\text{-}35}$ should be equal to two, whereas $\bar{\nu}_{S\text{-}35}$ approaches infinity in the case where the adsorption of oxygen is rate-controlling. Thus the estimate of $\bar{\nu}_{S\text{-}35}$ provides information as to the relative importance of the oxygen path or the sulfur path to the overall oxidation reaction.

III. DETERMINATION OF $\bar{\nu}_{S\text{-}35}$

Happel, Odanaka, and Rosche (*6*) made a mechanistic study of catalytic oxidation of sulfur dioxide with a commercially available vanadium pentoxide catalyst utilizing sulfur-35 as a tracer. The reaction temperature ranged from 460 and 480°C and the reaction pressure was about 1 atm. In Happel's investigation the ratio of the partial pressure of sulfur dioxide to that of oxygen in feed was varied rather widely. The apparent stoichiometric numbers $\bar{\nu}_{S\text{-}35}$ calculated for a variety of experimental conditions were approximately linearly correlated with the ratios of partial pressures of these component gases. The extrapolation of this linear relationship to zero value of the partial pressure ratio provides the estimate of $\bar{\nu}_{S\text{-}35}$ which corresponds to experimental conditions close to equilibrium. In the present work we re-estimated the value of $\bar{\nu}_{S\text{-}35}$ based on exact material balance of sulfur. Figure 1 shows the results. It was found that the estimate of $\bar{\nu}_{S\text{-}35}$ is 3.38 ± 0.21 instead of 2, which was previously reported by Happel, Odanaka, and Rosche (*6*). Note that ± signs of the estimate denote approximately 99% confidence limits. In view of the fact that the value of $\bar{\nu}_{S\text{-}35}$ is 2, when the sulfur path is rate-controlling, it may be con-

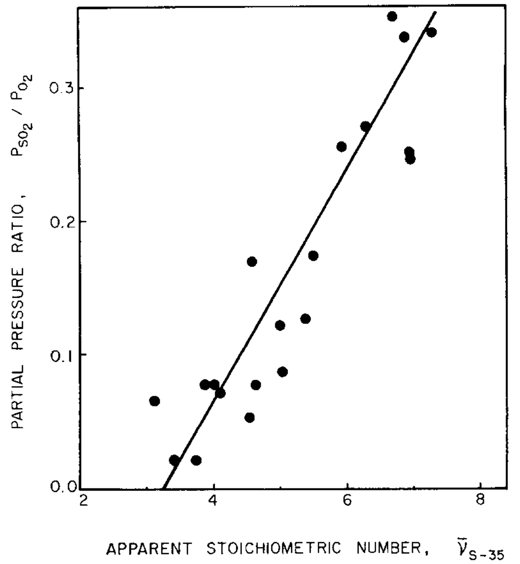

FIG. 1. Relationship between partial pressure ratio, p_{SO_2}/p_{O_2}, and the apparent stoichiometric number, $\bar{\nu}_{S-35}$.

cluded that the sulfur path influences the overall oxidation rate to a greater extent and the oxygen chemisorption has a smaller influence on the rate for experimental conditions close to chemical equilibrium.

IV. RATE MODELING OF THE OXIDATION REACTION

Rate equation (16) developed in the preceding section was employed to correlate an existing set of kinetic data. The data used was that gathered by Kadlec, Michalek, and Šimeček (*7*). We estimated rate parameters of Eq. (18) using only the data taken at temperatures between 380 and 480°C. At temperatures higher than 480°C, Kadlec, Michalek, and Šimeček (*7*) reported 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 sulfur dioxide and 11% of oxygen. The catalyst utilized was an ICI vanadium pentoxide catalyst. The maximum conversion of sulfur dioxide which Kadlec attained in his study was 84.4%.

For the formulation of $V_+^{1,3,4}$ of Eq. (16) we simply adopted a relationship similar to that proposed by Mars and Maessen (*8, 9*). This Mars–Maessen-type rate Eq. (17) was developed on the assumption that a step related to the oxygen adsorption is rate-controlling.

$$V = \frac{kKp_{SO_2}p_{O_2}}{[p_{SO_3}{}^{1/2} + (Kp_{SO_2})^{1/2}]^2} \times \left[1 - \left(\frac{p_{SO_3}{}^2}{p_{SO_2}{}^2 p_{O_2} K_p}\right)\right]. \quad (17)$$

The use of Eq. (17) leads to

$$V = \frac{kKp_{SO_2}p_{O_2}}{[p_{SO_3}{}^{1/2} + (Kp_{SO_2})^{1/2}]^2} \times \left[1 - \left(\frac{p_{SO_3}{}^2}{p_{SO_2}{}^2 p_{O_2} K_p}\right)^{[1-(1/\bar{\nu}_{S-35})]}\right], \quad (18)$$

where rate parameters, k and K, can be represented by the following forms:

$$k = A_1 e^{-E_1/RT}, \quad (19)$$

and

$$K = A_2 e^{+E_2/RT}. \quad (20)$$

Equation (18) possesses five parameters, including A_1, A_2, E_1, E_2, and $\bar{\nu}_{S-35}$. Evaluation of these five parameters was accomplished by means of nonlinear regression program. The objective function given by Eq. (21) was minimized with respect to the five rate parameters to obtain the best estimates of parameters:

$$\varphi = \sum_{i=1}^{N} \left(\frac{r_i - \hat{r}_i}{r_i}\right)^2. \quad (21)$$

Table 1 shows the resulting best estimates

TABLE 1
PARAMETER ESTIMATES FOR RATE EQUATIONS

Parameter	Eq. (17)[a]	Eq. (18)
A_1	7.34×10^{14}	7.34×10^{14}
E_1	4.72×10^4	4.71×10^4
A_2	1.17×10^{-9}	1.22×10^{-9}
E_2	2.73×10^4	2.72×10^4
$\bar{\nu}_{S-35}$	—	8.20
Sum of squares of residual rates	1.69×10^{-4}	1.62×10^{-4}

[a] Parameter estimates of Eq. (21) are taken from Ref. (*10*).

along with the parameter estimates of Eq. (17), which were reported in Ref. (*10*). Note that introduction of a parameter, $_{\mathrm{s-35}}$, provides virtually no changes on the estimates of parameters A_1, A_2, E_1, and E_2.

The adequacy of rate model of Eq. (18) was examined by two conventional statistical methods: examination of residual rates and analysis of variance. The results of these tests showed that the model is acceptable.

V. DISCUSSION

We now closely compare the rate model of Eq. (18) with Mars–Maessen-type model (*8, 9, 10*) in terms of the goodness-of-fit. As shown by Mezaki and Kadlec (*10*), a number of Mars–Maessen-type models can be set forth. Since result of an earlier investigation (*10*) indicated that a model given by Eq. (17) exhibited the best fit to Kadlec, Michalek, and Šimeček oxidation data (*7*) among a family of Mars–Maessen-type models, we used Eq. (17) for comparison. As can be seen from Table 1, the sum of squares of residual rates of Eq. (17) is not much different from that of Eq. (18). Because of the fact that more parameters are included in our model than in the Mars–Maessen-type model, one might conclude that the latter is superior over the former for the representation of Kadlec's data. However, a further comparison of data near equilibrium shown in Table 2 leads to the opposite conclusion. Average deviations from these rate models were computed by using exclusively the data points of conversions higher than 60%. As briefly described in a previous section, the value of $\bar{\nu}_{\mathrm{S-35}}$ has a marginal effect on rates calculated for experimental conditions removed from equilibrium. However, it improves substantially the goddness-of-fit of data at higher conversions. Thus the use of rate expression which includes a potential term with an apparent stoichiometric number seems vital to represent rate data at higher conversion.

TABLE 2
COMPARISON OF MARS–MAESSEN-TYPE MODEL AND OUR MODEL

	Av. deviation (%)
Mars–Maessen-model	26.11
Our model	16.59

As shown in Fig. 1 the value of $\bar{\nu}_{\mathrm{S-35}}$ depends on the experimental conditions, in particular, on the partial pressures of sulfur dioxide and oxygen. When a rate equation with $\bar{\nu}_{\mathrm{S-35}}$ is used to correlate rate data in which these partial pressures are widely changed and the relative importance of rate-controlling steps shifts from one step to another, an averaged value of $\bar{\nu}_{\mathrm{S-35}}$ would be obtained from a parameter estimation procedure. For the rate data gathered by Kadlec, the partial pressure ratio, $p_{\mathrm{SO_2}}/p_{\mathrm{O_2}}$, ranged approximately from 0.6 to 0.9. For this reason the estimate of $\bar{\nu}_{\mathrm{S-35}}$ turned out to be rather high.

Equation (16) was developed on the basis that steps (1) and (4) of Eq. (2) are both rate-controlling. For different reaction schemes of the sulfur dioxide oxidation reaction similar rate expressions would be obtained. If we assume that steps (1) and (2) control the oxidation rate, for example, the foregoing mathematical procedure yields

$$V = V_{+}{}^{1,3,4}\left(1 - \frac{p_{\mathrm{SO_3}}{}^2}{p_{\mathrm{SO_2}}{}^2 p_{\mathrm{O_2}} K_p}\right)^{[1-(2/\bar{\nu}_{\mathrm{S-35}})]}. \tag{22}$$

Equation (22) would perhaps be appropriate for the case wherein very dilute sulfur dioxide is oxidized under an atmosphere rich in oxygen. It is evident from Eqs. (16) and (22) that the exponent in the potential term can be a fractional number, depending upon the relative dominance of controlling steps of the oxidation reaction.

It appears that the model of Eq. (18) has a great promise to describe rate data gathered near chemical equilibrium. The estimate of $\bar{\nu}_{\mathrm{S-35}}$ would be close to 2 if a step of the sulfur path overwhelmingly controls the oxidation rate in the vicinity of equilibrium. For such non-linear models as that given by Eq. (18) it is generally difficult to obtain the precise estimates of parameters. As discussed earlier an independent experiment with isotopic tracers could provide the estimate of $\bar{\nu}_{S-35}$, simplifying substantially the estimation procedure of parameters. Equation (18) is quite adequate to describe the rate data taken in experimental conditions similar to those of Kadlec's study. Further analysis must be performed in order to fully test the usefulness of Eq. (18) for data taken closer to chemical equilibrium.

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