Kinetics of the Catalytic Oxidation of Sulfur Dioxide

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The establishment of the rate controlling step for the oxidation of sulfur dioxide in the presence of supported catalysts of platinum and vanadium has been the subject of both considerable interest and controversy. Experimental studies with platinum supported catalysts were reported in the early work of Bodenstein and Fink (*2*), who concluded that their data could be correlated by the following expression:

$$r = k \frac{p_{SO_2}}{\sqrt{p_{SO_3}}} \qquad (1)$$

In 1927 Lewis and Ries (*15*) obtained oxidation data using a platinum catalyst supported on asbestos and proposed that the kinetics for this reaction could be represented by the relationship

$$r = k\, p_{SO_2} \ln \frac{(p_{SO_3})_\epsilon\,(p_{SO_2})}{(p_{SO_2})_\epsilon\,(p_{SO_3})} \qquad (2)$$

where $(p_{SO_3})_\epsilon$ and $(p_{SO_2})_\epsilon$ represent equilibrium conditions. Further studies with platinum catalysts have been reported by Taylor and Lenher (*18*), Boreskov (*3*), Hurt (*13*), and more recently by Olson, Schuller, and Smith (*16*).

The reaction kinetics for the catalytic oxidation of sulfur dioxide with a commercial grade of vanadium pentoxide catalyst have been studied as early as 1937 by Boreskov and Sokolova (*4*), who concluded that the rate of this oxidation reaction can be represented by the following relationship:

$$r = k \frac{p_{SO_2}^{0.8}\, p_{O_2}}{p_{SO_3}} \qquad (3)$$

Krichevskaya (*14*) reported in 1947 that the oxidation of sulfur dioxide over a commercial vanadium pentoxide catalyst could be represented by the following expression:

$$r = k \sqrt{p_{SO_2}\, p_{O_2}} \qquad (4)$$

Using a vanadium pentoxide catalyst Calderbank in 1952 performed independent studies on the kinetics of this reaction and on the adsorption equilibrium of the components of this reaction to establish the temperature dependence of the rate of reaction (*5*). He found that the kinetics of this reaction could be represented by a power law expression of the form

$$r = k\, p_{SO_2}^{m}\, p_{O_2}^{n} \qquad (5)$$

where m varies from 0.35 to 0.56 and n from 0.720 to 0.500 in the temperature range 370° to 420°C. From these studies it was concluded that the rate determining step involves chemisorbed sulfur dioxide and oxygen in the gas phase to produce chemisorbed sulfur trioxide.

Baron, Johnstone, and Manning (*1*) impregnated the inside surface of an alundum cylinder with a potassium metavanadate catalyst. They studied the effects of inert gases on the rate of reaction, with the assumption that the kinetics for this reaction could be described by a pseudo first-order expression of the type

$$r = k\, p_{SO_2} \qquad (6)$$

In the recent experimental study of Goldman, Canjar, and Beckmann (*10*) on the oxidation kinetics of sulfur dioxide over a vanadium catalyst in the temperature range 375° to 430°C. the approach suggested by Hougen and Watson (*12*) was utilized to represent the rate controlling step as

$$r = \frac{C\,[p_{SO_2}\sqrt{p_{O_2}} - p_{SO_3}/K]}{[1 + K_{SO_2}\,p_{SO_2} + K_{O_2}^{1/2}\,p_{O_2}^{1/2} + K_{SO_3}\,p_{SO_3}]^2} \qquad (7)$$

The reaction velocity constant and associated adsorption equilibrium constants determined by Goldman et al. (*10*) were found to correlate linearly with temperature in accordance with the Arrhenius theory.

Hara, Adachi, and Kurata (*11*) investigated this reaction in the range 400° to 550°C. over a similar catalyst and also applied the Hougen and Watson approach to analyze their data. They concluded that the rate control-

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ling step was in agreement with that postulated by Goldman et al. In all existing studies, and in particular those of Goldman, Canjar, and Beckmann (*10*) and Hara, Adachi, and Kurata (*11*), the effect of the presence of nitrogen has not been included in the adsorption term of the denominator of Equation (7).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A differential bed reactor, confined in a cylindrical stainless steel tube (type 316 SS) 36 in. long and having an inside diameter of 0.896 in., was used to obtain the kinetic data at 643°, 672°, and 722°F. and 1.47 atm. Eight runs were conducted at each temperature level. The details of the experimental unit and differential bed reactor are included in Figure 1. The catalyst was included in the reactor, which was 10 in. in length.

Preparation of Catalyst Pellets

The catalyst used was specifically designed to eliminate intraparticle diffusion by confining the reaction to occur on the surface of each spherical pellet. The catalyst consisted of inert alumina-silica spheres, 3/16 in. in diameter, whose external surfaces were coated with a thin layer of a commercial vanadium pentoxide catalyst. This active catalyst was promoted with potassium oxide and was impregnated throughout a diatomaceous silica support. Pellets of this catalyst were then pulverized, and the dry powder was made to adhere to the outside surface of the alumina-silica spheres that had been completely soaked with water. These spheres were then dried, and the process was reversed by rolling them in the catalyst powder, which was slightly moistened. The coated spheres were again dried, and this latter process was again repeated until an adequate amount of catalyst surrounded each sphere. For a catalyst bed of 925 spheres 10.2 g. of active catalyst was supported on them. The catalyst powder has a yellow to yellowish brown color in its highest oxidation state and had the following specifications:

	Weight %
V_2O_5	7.35- 9.35
K_2O	9.0 -11.0
Fe	0.5
Diatomaceous silica	Approx. 80

The average bulk density of the catalyst powder was 0.70 g./cc. The maximum thickness of the catalyst covering each sphere was calculated from the weight of catalyst per sphere and the bulk density value to be less than 0.05 in. A visual inspection of cross-sectional cuts of representative spheres indicated that the depth of catalyst penetration was confined only to the peripheral surface of each sphere.

Catalyst Pretreatment

Before the experimental program was initiated, a long blank run was carried out at 750°F. with no catalyst present. No noticeable reaction was observed as indicated from a material balance on sulfur dioxide. To obtain consistency in catalytic activity at the beginning of each experimental run the temperature of the catalyst was raised to 750°F. in the presence of air. This procedure insured that the oxidation state of the catalyst was at its highest value. Subsequent to this pretreatment sulfur dioxide was introduced into the air stream. At the conclusion of each run the unit and reactor were purged with nitrogen overnight before the procedure already presented was repeated.

Experimental Procedure

A long, narrow bed was used because it serves to eliminate the effects of back mixing and tends to smooth out radial and axial temperature gradients. The void fraction of the catalyst was $\epsilon = 0.400$, which permitted small pressure drops to exist at the higher mass velocities. In order to balance properly the inlet temperature and minimize the holdup time the reactor bed was included between 8 in. of inert catalyst support above the bed and 18 in. below the bed. Good temperature control was effected with four independently operated heating elements and a jacket, in which the hot gases leaving the reactor were made to flow countercurrently to it. Isothermal conditions at the inlet and outlet of the catalyst bed were obtained by manually controlling the different powerstats of the reactor bed. The temperature was measured with 28 gauge chromel-alumel thermocouples which were attached to a twenty-four point temperature recorder. These thermocouples were calibrated with boiling water and molten lead and zinc and were capable of measuring temperatures within 1°C. In order to avoid irregularities in the flow pattern through the catalyst bed no attempt was made to insert a thermowell inside the catalyst bed itself for an indication of possible axial and radial temperature gradients. Since the inlet and outlet temperatures of the reactor were made to be within 1°C., it is a fair assumption to neglect the effect of axial and radial temperature gradients in this study. The combination of low temperature and high mass velocities permitted this reactor to operate as a differential bed. In the majority of the runs less than 15% conversion was obtained.

Feed compositions were prepared by the simultaneous mixing of extra dry research grade air, nitrogen, sulfur dioxide, and oxygen gases. Each of these constituents was maintained at a compressed state in high-pressure gas cylinders, which were pressure regulated with a two-stage regulator and needle valve. Glass capillary flow meters were used to determine the flow rate of each gas. To insure proper mixing the sulfur dioxide was introduced into the vena contracta of an orifice plate. The premixed feed stream was passed through a preheater, which was heated to within ± 20°C. of the reactor temperature. The preheater consisted of a 1½-in. standard stainless steel pipe, 3 ft. long, which was packed with ¼-in. ceramic saddles. This preheater was externally heated with three independently controlled heating elements.

The effluent stream leaving the reactor was for the most part discharged to the vent through a downstream pressure control valve. The remaining small portion was passed through a water-cooled stainless steel tubing and then through a sulfur-trioxide scrubber consisting of a train of three fritted gas bubblers provided with 98% sulfuric acid. A portion of the stream leaving the sulfur-trioxide scrubber was withdrawn for analysis.

The composition of the effluent gases was determined on a sulfur trioxide-free basis. The analytical equipment consisted of a modified Orsat unit, and the sulfur dioxide content was determined by absorbing this constituent into a dilute hydrogen peroxide solution. From a knowledge of the sulfur dioxide content of the inlet and effluent streams a complete material balance was made for each run, which was based on nitrogen as the tie element. The feed inlet composition for each run was cross checked with the metered flow rates of the individual reactants and the results of the Orsat gas analysis.

TREATMENT OF EXPERIMENTAL DATA

Fundamental Approach

Reaction rates were established from the material balance for each run. This information was used to determine the contributions of mass transfer by the use of the method proposed by Yang and Hougen (*21*). The resulting information indicated that mass transfer contributions should not be neglected. In order to determine interfacial compositions the contributions due to mass transfer for each component were calculated by the use of the following relationship for the mass transfer factor (*17*):

$$\epsilon j_d = \frac{2.06}{N_{Re}^{0.575}} \tag{8}$$

These calculations were conducted in the manner outlined by Hougen and Watson (*12*) for a related problem dealing with the oxidation of sulfur dioxide. Main stream compositions for representative runs are presented in Table 1 along with the corresponding instantaneous rates, mass velocities, and conversions. The experimental data and derived quantities are presented for the twenty-four runs elsewhere (*7*).

Previous work concerned with this reaction has indicated that a plausible rate controlling step is a surface re-

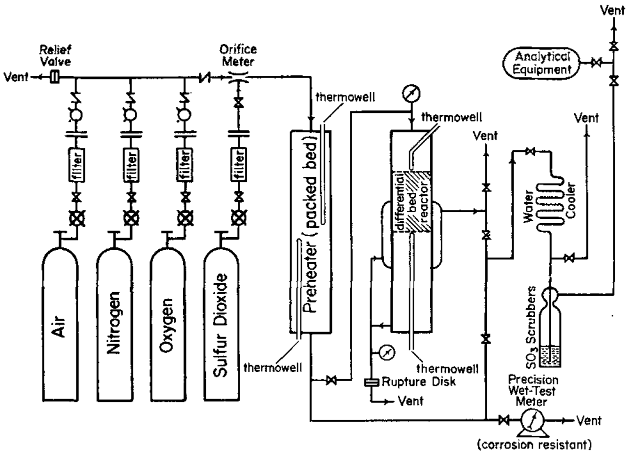

Fig. 1. Schematic diagram of experimental equipment.

action involving chemisorbed sulfur dioxide and chemisorbed atomic oxygen (*11*, *19*). For this postulated rate controlling step it can be shown that the rate of reaction, in the presence of nitrogen as a diluent, can be expressed as

$$r = \frac{C\,[p_{SO_2}p_{O_2}^{1/2} - p_{SO_3}/K_p]}{[1 + K_{SO_2}p_{SO_2} + \sqrt{K_{O_2}p_{O_2}} + K_{SO_3}p_{SO_3} + K_{N_2}p_{N_2}]^2} \qquad (9)$$

where $C = Ek_sSLK_{SO_2}K_{O_2}^{1/2}$; K_{SO_2}, K_{O_2}, K_{SO_3}, K_{N_2} are adsorption equilibrium constants, K_p is the equilibrium constant of the reaction, and p represents the interfacial partial pressure of each component.

Uyehara and Watson (*19*) analyzed the catalytic oxidation data of Lewis and Ries (*15*), who conducted a series of flow experiments in reactors approximating differential bed conditions. A platinized asbestos catalyst was used by them in glass U-tube reactors immersed in a molten metal bath. A careful examination of the data led Uyehara and Watson to conclude that these data could be best represented by the following rate controlling step:

$$r = \frac{C\,[p_{SO_2}p_{O_2}^{1/2} - p_{SO_3}/K]}{[1 + \sqrt{K_{O_2}p_{O_2}} + K_{SO_3}p_{SO_3}]^2} \qquad (10)$$

For this postulated rate controlling step the denominator should include terms for each of the participating reactants and products. In their study Uyehara and Watson excluded from the denominator the term, $K_{SO_2}p_{SO_2}$ and followed the suggestion of Bodenstein and Fink (*2*) that the concentration of nitrogen and other various inerts did not affect the rate of oxidation; therefore they eliminated the nitrogen term $K_{N_2}p_{N_2}$. Calderbank (*5*) used pure nitrogen over a vanadium pentoxide catalyst and concluded that the adsorption of nitrogen on the catalyst is negligible in a nonreacting system. Goldman et al. (*10*) and Hara et al. (*11*) applied this conclusion of Calderbank to their oxidation studies by eliminating the nitrogen adsorption term $K_{N_2}p_{N_2}$. This presupposes that the adsorption of nitrogen in a multicomponent reacting system is the same for a system involving pure nitrogen. Clark and Berets (*6*) point out that catalysts under isolated conditions differ vastly in behavior from those occurring in active catalytic reactions.

Because of these considerations it was thought advisable to subject the experimental data of this study to an analysis that assumes that each component contributes to the rate of reaction. For the reaction

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad (11)$$

Evans and Wagman (*8*) present the following relationship for the equilibrium constant of this reaction:

$$\log_{10} K_p = \frac{4{,}956}{T,\ ^\circ K.} - 4.678 \qquad (12)$$

where $K_p = p_{SO_3}/p_{SO_2}p_{O_2}^{1/2}$. For the temperature range of the present study, 643°F. (613°K.) to 722°F. (657°K), this equilibrium constant ranges from $K_p = 2{,}550$ to $K_p = 733$, respectively. Since the average partial pressures of sulfur trioxide in the experimental runs of this study are always less than 0.01 atm., the reverse reaction can be neglected. Therefore Equation (9) can be rearranged as follows:

$$R = \frac{1}{\sqrt{C}}\;\frac{K_{SO_2}}{\sqrt{C}}p_{SO_2} + \frac{\sqrt{K_{O_2}}}{\sqrt{C}}p_{O_2}^{1/2} + \frac{K_{SO_3}}{\sqrt{C}}p_{SO_3} + \frac{K_{N_2}}{\sqrt{C}}p_{N_2} \qquad (13)$$

where $R = \sqrt{p_{SO_2}p_{O_2}^{1/2}/r}$. Equation (13) is linear in four independent variables. The coefficients of these variables can be established either by a least-squares approach or by graphical means. The application of the method of least squares to establish these coefficients does not readily lend itself to this study, since only eight runs are available at each temperature level. In order to utilize each set of eight runs effectively the graphical approach was used to establish each coefficient of Equation (13).

The coefficients of Equation (13) can be readily evaluated if data are available in which the rates are measured while the concentration of one component is varied, holding all others constant. However the exact attainment of such conditions is not practical, since this would require advance knowledge of the exact effect of all the variables controlling the reaction rates. Nevertheless a plot of R vs. the partial pressure of any one of the components will yield a group of points. Any two or more points, which can be associated with similar concentrations of the other

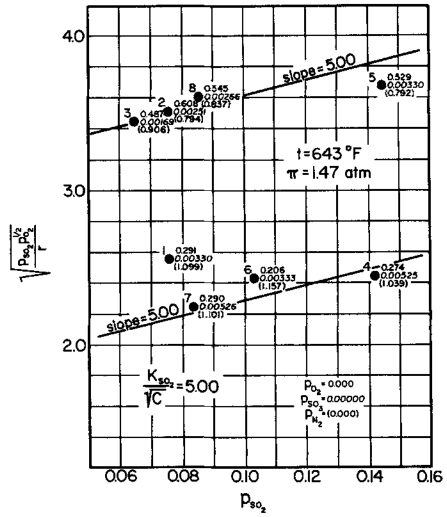

Fig. 2. Dependence of $\sqrt{p_{SO_2}\;p_{O_2}^{1/2}/r}$ on p_{SO_2} at 643°F. and 1.47 atm.

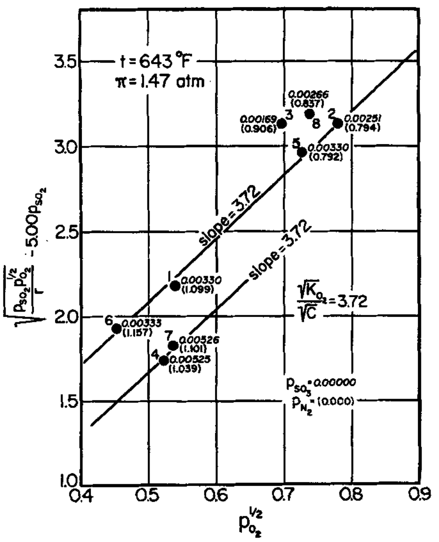

Fig. 3. Dependence of $\sqrt{p_{SO_2}\, p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2}$ on $p_{O_2}^{1/2}$ at 643°F. and 1.47 atm.

components, will yield the linear dependence of *R* on the partial pressure of that component.

The data points at 643°F. are plotted as *R* vs. p_{SO_2} in Figure 2. It is observed that in this group of points runs 4 and 7 have similar concentrations of oxygen, sulfur trioxide, and nitrogen. Therefore a straight line of positive slope $K_{SO_2}/\sqrt{C} = 5.0$ passing through the vicinity of these two points should represent in a reasonable manner the dependence of $\sqrt{p_{SO_2} p_{O_2}^{1/2}}/r$ on p_{SO_2}. The positive intercept of this line is also consistent on physical grounds.

Likewise runs 2, 3, 5, and 8 can be treated in essentially the same manner to produce a straight line whose slope is also positive and equal to 5.0. This analysis leads to the strong inference that the quantity $K_{SO_2}/\sqrt{C} \approx 5.0$, and therefore this procedure can be extended by the elimination of the influence of sulfur dioxide by plotting $\sqrt{p_{SO_2} p_{O_2}^{1/2}}/r - 5.00\, p_{SO_2}$ against the partial pressure of oxygen, nitrogen, or sulfur trioxide. Figure 3 presents a group of points for this temperature when $\sqrt{p_{SO_2} p_{O_2}^{1/2}}/r - 5.00\, p_{SO_2}$ is plotted against $p_{O_2}^{1/2}$. Runs 1 and 6 have essentially the same partial pressures of sulfur trioxide and nitrogen and yield a straight line whose slope is $\sqrt{K_{O_2}}/\sqrt{C} = 3.72$ and which also has a positive intercept. This line when extended passes through the points corresponding to runs 2 and 5. Similarly runs 4 and 7 can be fitted to a line parallel to the previous one. Thus the effect of oxygen can be accounted for through the coefficient. $\sqrt{K_{O_2}}/\sqrt{C} = 3.72$. When the oxygen contribution is accounted

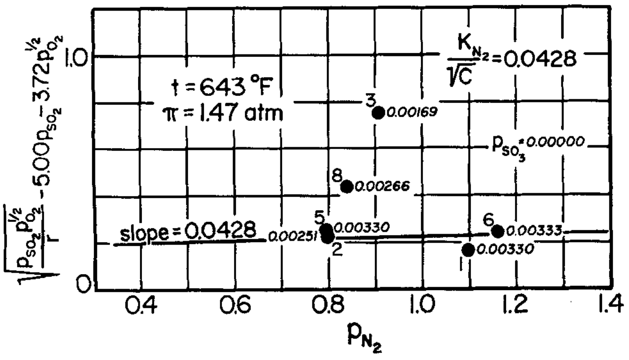

Fig. 4. Dependence of $\sqrt{p_{SO_2}\, p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2} - 3.72\, p_{O_2}^{1/2}$ on p_{N_2} at 643°F. and 1.47 atm.

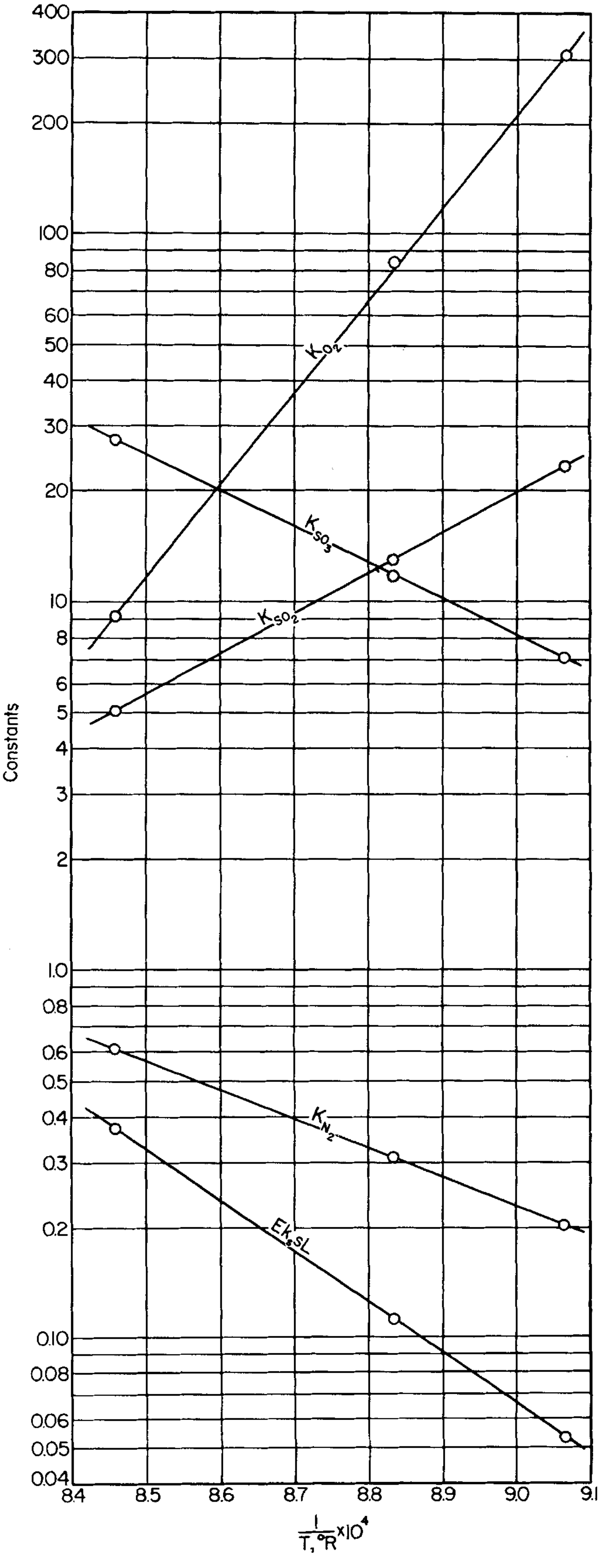

Fig. 5. Relationships between constants and reciprocal absolute temperature.

TABLE 1. EXPERIMENTAL DATA FOR REPRESENTATIVE RUNS IN THE CATALYTIC OXIDATION OF SULFUR DIOXIDE

Run	G, lb./hr·× sq. ft.	Average partial pressures in main stream, atm.				r_A, lb.-moles of SO_3 formed / hr. × lb· of catalyst	x_A, lb.-moles of SO_2 converted / lb.-mole of SO_2 in feed × 100
		SO_3	SO_2	O_2	N_2		
				t = 643°F.	π = 1.47 atm.		
1	228	0.00319	0.0758	0.291	1.100	0.00627	8.05
4	301	0.00506	0.142	0.274	1.040	0.0125	6.83
7	206	0.00511	0.0838	0.290	1.101	0.00895	11.5
				t = 672°F.	π = 1.47 atm.		
9	228	0.00702	0.0720	0.289	1.102	0.0138	17.8
12	301	0.00824	0.139	0.273	1.041	0.0203	11.3
16	211	0.00744	0.0808	0.544	0.838	0.0131	16.7
				t = 722°F.	π = 1.47 atm.		
17	228	0.00897	0.0702	0.289	1.103	0.0176	21.6
20	301	0.0112	0.136	0.271	1.040	0.0276	15.2
24	211	0.00899	0.0793	0.543	0.839	0.0158	20.3

for, the effect of the concentration of nitrogen can be established by plotting $\sqrt{p_{SO_2}p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2} - 3.72\, p_{O_2}^{1/2}$ vs. p_{N_2}. The results of this analysis in Figure 4 indicate that an essentially horizontal line can represent the dependence of $\sqrt{p_{SO_2}p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2} - 3.72\, p_{O_2}^{1/2}$ on the partial pressure of nitrogen for nearly constant partial pressures of sulfur trioxide. The straight line of this figure is based on runs 1, 2, 5, and 6, and its slope is slightly positive and equal to $K_{N_2}/\sqrt{C} = 0.0428$.

This iterative procedure was continued to account for the presence of sulfur trioxide by plotting the group $\sqrt{p_{SO_2}p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2} - 3.72\, p_{O_2}^{1/2} - 0.0428\, p_{N_2}$ vs. p_{SO_3}. Six of the eight runs at this temperature of 643°F. produced differences which were positive and which have been represented by a straight line of slope $K_{SO_3}/\sqrt{C} = 1.50$. At 672°F. five of the eight runs produced positive differences, while at 722°F. all eight runs produced positive differences. The good agreement at this highest temperature corresponding to high conversions undoubtedly is the result of the random error in the analytical equipment and procedure used, which is relatively less significant than the corresponding error at the lower temperatures, where the conversions are lower.

When one uses the coefficients $K_{SO_2}/\sqrt{C} = 5.00$, $\sqrt{K_{O_2}}/\sqrt{C} = 3.725$, $K_{N_2}/\sqrt{C} = 0.0428$, and $K_{SO_3}/\sqrt{C} = 1.50$, the effective intercept $1/\sqrt{C}$ is determined by calculating the residual of the quantity $\sqrt{p_{SO_2}p_{O_2}^{1/2}/r} - 5.00\, p_{SO_2} - 3.72\, p_{O_2}^{1/2} - 0.0428\, p_{N_2} - 1.50\, p_{SO_3}$ for each run. For the six runs the following positive values of $1/\sqrt{C}$ resulted:

Run	$1/\sqrt{C}$
1	0.113
2	0.189
4	0.699
5	0.203
6	0.169
8	0.387

The average value of these runs (excluding the somewhat high value of run 4) produced $1/\sqrt{C} = 0.212$, making $C = 22.25$. Therefore the corresponding adsorption equilibrium constants at 643°F. become $K_{SO_2} = 23.58$, $K_{O_2}^{1/2} = 17.57$, $K_{N_2} = 0.202$, and $K_{SO_3} = 7.08$. Since $C = Ek_sSLK_{SO_2}K_{O_2}^{1/2}$, it follows that $Ek_sSL = 0.0537$.

Similarly values of C, K_{SO_2}, $K_{O_2}^{1/2}$, K_{SO_3}, and K_{N_2} were established at 672° and 722°F. The summarized values of these calculated constants are as follows:

	643°F.	672°F.	722°F.
C	22.25	13.39	5.67
K_{SO_2}	23.58	13.2	5.07
$\sqrt{K_{O_2}}$	17.57	9.14	3.02
K_{SO_3}	7.08	11.7	27.4
K_{N_2}	0.202	0.310	0.612
Ek_sSL	0.0537	0.111	0.370

Each constant was plotted against the reciprocal absolute temperature in accordance with the Arrhenius theory to produce the linear relationships presented in Figure 5. These results show that these straight lines have positive and negative slopes, indicating that both endothermic and exothermic heats of reaction are involved in the chemisorption steps. This temperature dependence is in line with the theory of absolute reaction rates (9), and the constants can be expressed analytically as follows:

$$C = e^{\frac{44{,}900}{RT} - \frac{34.51}{R}} \tag{14}$$

$$K_{SO_2} = e^{\frac{50{,}400}{RT} - \frac{39.42}{R}} \tag{15}$$

$$\sqrt{K_{O_2}} = e^{\frac{57{,}750}{RT} - \frac{46.6}{R}} \tag{16}$$

$$K_{SO_3} = e^{-\frac{44{,}400}{RT} + \frac{44.13}{R}} \tag{17}$$

$$K_{N_2} = e^{-\frac{36{,}350}{RT} + \frac{29.773}{R}} \tag{18}$$

and

$$Ek_sSL = e^{-\frac{63{,}300}{RT} + \frac{51.60}{R}} \tag{19}$$

Equations (14) through (19) have been used to calculate all the constants of Equation (9), used to calculate reaction rates for the conditions of each run. For the twenty-four runs of this study a comparison between calculated and experimental rates produced deviations of 6.90% at 643°F., 25.0% at 672°F., and 15.6% at 722°F., the overall average deviation being 15.8%.

Empirical Approach

From the interfacial compositions presented in Table 1 a general power law expression of the form

$$r = kp_{SO_2}^{n}p_{O_2}^{m} \tag{20}$$

suggested by Weller (*20*) was used to correlate the data of each temperature level. To maintain the form of this empirical rate expression consistent with those of Calderbank (*5*), Krichevskaya (*14*), and Baron, Johnstone, and Manning (*1*) the influence of sulfur trioxide and nitrogen has not been included in Equation (20). When one employs the least-squares method, the following best values of k, m, and n corresponding to 643°, 672°, and 722°F. result:

	643°F.	672°F.	722°F.
k	0.0322	0.0488	0.0795
m	−0.500	−0.128	0.000
n	0.871	0.662	0.617

These numerical values of k and m increase with increasing temperature, while the values of exponent n decrease with increasing temperature. Thus the rate of reaction undergoes a change from $r = 0.0322\, p_{SO_2}^{0.871}/p_{O_2}^{1/2}$ at 643°F. to $r = 0.0795\, p_{SO_2}^{0.617}$ at 722°F. Such behavior complicates the interpretation of fundamental kinetic studies, since the form of the general power-law expression changes with temperature. Despite these shortcomings reaction rates calculated at 643°, 672°, and 722°F. with these constants have been compared with corresponding experimental values to produce deviations of 12.8% at 643°F., 25.0% at 672°F., and 12.9% at 722°F.

CONCLUSIONS

The Hougen and Watson approach (*12*) has been applied to the analysis of kinetic data obtained for the catalytic oxidation of sulfur dioxide over a commercial vanadium pentoxide catalyst. The results indicate that the rate-controlling step involves a surface reaction between chemisorbed sulfur dioxide and chemisorbed atomic oxygen to produce chemisorbed sulfur trioxide and a vacant site. Furthermore this approach directly accounts for the presence of all the reacting and product constituents, including nitrogen. The temperature dependence of the resulting reaction velocity constant and adsorption equilibrium constants has been found to be consistent with the theory of absolute reaction rates. Because of the good agreement resulting between experimental rates and values calculated with the rate expression corresponding to this surface reaction, no other approaches of this type have been considered.

Although a power-law expression is capable of predicting rates with essentially the same degree of accuracy, its application must be limited to the range of conditions of the experimental data used to develop this expression.

The use of completely empirical rate expressions for the study of heterogeneous reactions while expedient in application, does not contribute to the understanding of the fundamental nature of reactions occurring on catalytic surfaces. On the other hand the theoretically based steps of Hougen and Watson give rise to a model that produces compatible consequences that are of a more basic nature and bridge the gap between complete empiricism and the complex adsorption interactions and chemical reactions occurring on the surface of the catalyst.

Although the Hougen and Watson approach includes certain inherent weaknesses, it does however offer to date the most comprehensive approach to this subject. Attempts to improve on this model should constitute an advancement for the better understanding of the mechanics of catalytic reactions. The substitution of expedient empirical expressions, although capable of meeting the immediate needs for reactor design, unfortunately does not contribute to the basic understanding of heterogeneous reaction kinetics.

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NOTATION

C = reaction velocity constant
D_p = catalyst particle diameter, ft.
E = effectiveness factor
G = superficial mass velocity, lb./hr. sq. ft.
j_d = mass transfer factor
k = apparent reaction velocity constant
k_s = reaction velocity constant for surface reaction
K = adsorption equilibrium constant
K_p = equilibrium constant, $p_{SO_3}/p_{SO_2}p_{O_2}^{1/2}$, $1/(\text{atm.})^{1/2}$
L = total number of active sites
m, n = exponents for power-law expressions
N_{Re} = Reynolds number, D_pG/μ
p = partial pressure, atm.
r = reaction rate, lb.-moles/hr. × lb. of catalyst
R = gas constant, 1.987 cal./g.-mole °K.
R = $\sqrt{p_{SO_2}p_{O_2}^{1/2}/r}$
s = number of adjacent active sites
T = absolute temperature
ϵ = void fraction of packed bed
μ = viscosity, lb./hr. ft.

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