

Diluent Gas Effect in Catalytic SO₂ Oxidation

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Received March 28, 1975

The effects of SO₂ and O₂ partial pressure and total molar flow with different inert diluents were studied on the initial oxidation rate of SO₂ over a vanadia catalyst. Argon and helium were used separately as diluents. In all but one run, an enhanced reaction rate was observed with argon at 405°C. An unexpected effect of reactant composition on the magnitude of the inert gas influence was found; the greatest influence of the inert gas appeared at low SO₂/O₂ ratios.

NOMENCLATURE

F	variance ratio
x_1	function of X_1 in Eq. (1)
x_2	function of X_2 in Eq. (1)
X_1 , etc.	code for independent variable; see Table 1
Y	code for the dependent variable; see Table 1
z_1	function of X_2 in Eq. (2)
z_2	function of X_2 in Eq. (2)
σ^2	true value of the error variance
$\hat{}$	predicted value
Ar	value obtained using argon as a diluent gas
He	value obtained using helium as a diluent gas.

INTRODUCTION

The oxidation of SO₂ over vanadium pentoxide catalyst exhibits a curious dependence on the diluent gas used in the feed gas mixture. Baron *et al.* (1) first reported this phenomenon in which the reac-

tion rate increased with increasing molecular weight of the diluents (He, N₂, CO₂) while the activation energy decreased. Recently, Yeramian *et al.* (2) corroborated this phenomenon in a lower temperature range with an industrial V₂O₅ catalyst using as diluent two noble gases (He and Ar) and nitrogen. In both of these studies experiments were made at a constant partial pressure of SO₂, O₂, and diluent over a range of temperatures.

Current models of heterogeneous catalytic reactions do not anticipate a diluent gas effect; the phenomena responsible are unknown despite an appreciable research effort and are likely to be complex. In this situation our strategy has been to map conditions under which the diluent effect is encountered. It was the object of this study to discover whether the diluent gas affects the rate equally over a range of compositions of reactants and product.

Since the effect could be small, a statistical approach was taken. The experimental apparatus and procedure first used by Yeramian (3) were adopted.

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DESIGN OF EXPERIMENTS

Since it is well established that the rate of oxidation of SO₂ depends upon the partial pressures of SO₂, O₂, and SO₃ (3-7), it was decided to perform two sets of experiments identical in partial pressures of SO₂, O₂, and inert gas and in space velocity but differing in the species of inert gas used. Space velocity was introduced as a variable because SO₃ partial pressure would be proportional to it and furthermore its variation permitted the investigation of interparticle mass and heat transfer. The explanation of Baron *et al.* (1) that the diluent gas effect was a molecular weight effect made it reasonable to select argon (MW 39.95) and helium (MW 4.00) to gain a large molecular weight difference.

The temperature for the experiments was chosen as 405°C, in the middle of the range in which Yeramian *et al.* (2) had found a substantial inert gas effect.

Since second-order dependencies on the partial pressures of reactants were expected, a central composite design was chosen of the type described by Peng (8). The design permitted the near-optimal estimation of second-order interactions and main effects. To obtain a good estimate of the error variance, σ^2 , the factorial design within the composite and the center points were replicated. For runs with argon as the diluent gas, all three variables: p_{SO_2} , p_{O_2} ,

and total molar flow were varied. Tables 1 and 2 indicate the actual levels of the variables used in the argon experiments and the order of runs. The same catalyst sample was used in all runs.

EXPERIMENTAL TECHNIQUE

A differential reactor operating at about 1 atm and set in a bed of heated, fluidized sand, was used for the study. Details are given in an earlier paper by Yeramian *et al.* (2). As in the earlier work, Cyanamid Aero SA vanadia catalyst was used; however, a 30/40 U.S. mesh size was employed.

In operating the reactor, the temperature was set for the run by bringing the fluidized sand bath to 410°C, initiating the SO₂ and O₂ flows and then reducing the temperature to 405°C. This procedure was followed because of the observation of Malin (9) that vanadia catalysts when used for the oxidation of SO₂ exhibit hysteresis, the reaction rate being higher when reached by cooling than by heating. This procedure reduced the time required before steady state was attained.

Reaction conditions were maintained closely during runs. After rates were within about 10% of one another on successive runs an hour apart, steady state was assumed and a rate measurement made after a further hour on stream. In

TABLE 1
CODE DEFINITIONS USED IN EXPERIMENTAL DESIGN

Variable	Code level				
	-1.633	-1	0	1	1.633
Y reaction rate mmol SO ₃ formed/h - g catalyst					
X ₁ mole fraction of SO ₂ in feed gas	0.040	0.0710	0.120	0.169	0.200
X ₂ mole fraction of O ₂ in feed gas	0.050	0.0985	0.175	0.252	0.300
X ₃ total molar flow of feed gas	0.80	1.11	1.60	2.09	2.40

TABLE 2
EXPERIMENTAL DESIGN AND RESULTS FOR
RUNS USING ARGON AS DILUENT

Run	X_1	X_2	X_3	Y_{Ar}
1	-1	-1	1	1.81
2	1	-1	-1	2.52
3	-1	1	-1	2.40
4	1	1	1	3.50
5	-1	-1	-1	2.01
6	1	-1	1	2.75
7	-1	1	1	2.75
8	1	1	-1	3.46
9	-1	-1	1	2.01
10	1	-1	-1	2.75
11	-1	1	-1	2.52
12	1	1	1	3.34
13	-1	-1	-1	1.89
14	1	-1	1	2.44
15	-1	1	1	2.60
16	1	1	-1	3.34
17	-1.633	0	0	1.73
18	1.633	0	0	2.67
19	0	-1.633	0	1.06
20	0	1.633	0	3.93
21	0	0	-1.633	2.36
22	0	0	1.633	2.48
23	0	0	0	2.44
24	0	0	0	2.28

practice this meant waiting for up to 6 hr after setting new conditions using argon and up to 10 hr using helium. In addition, with fresh catalyst, 45 hr on stream were required to reduce the catalyst activity to a stable value. To shut down the reactor, SO_2 and O_2 flows were stopped while inert gas purged the system. The sand bath was regulated at $200^\circ C$ to prevent possible condensation of SO_3 on the catalyst surface with the possibility of a change in its activity (4).

The sampling and wet chemical technique used to measure SO_3 in the off gas from the reactor was a variation of that used by Yeramian. Conversion of SO_2 and reaction rate of SO_2 were calculated from the SO_3 concentration. Details of the technique and calculations are given by Rhodney (10).

The wet chemical technique was tested by comparing the root mean square (rms)

deviation from a known standard (sulfuric acid) with the error standard deviation of replicated analyses on the same unknown SO_3 sample. The rms deviation was found to be 2.1% and the error standard deviation to be 1.54%. A t test for bias, which had sufficient power to detect a bias of 2.5% with high probability, failed to detect any bias in the analytical method. We therefore had an accurate and reproducible measurement technique.

RESULTS

Preliminary analysis of the argon data showed that these data could be satisfactorily fitted by a model that did not contain the variable X_3 (flow rate). This variable was subsequently omitted in the runs made with helium, reducing the number of independent variables by one. The design was thence modified to that shown in Tables 2 and 3. However, when the quadratic model implied in the design was used, there was significant lack of fit as determined by analysis of variance. Consequently, a transformation of the independent variables was used, as described in Appendix 1. After this operation a satisfactory fit was accomplished.

INTERPRETATION

The lack of dependency of the reaction rate on the ratio of catalyst weight to flow

TABLE 3
EXPERIMENTAL DESIGN AND RESULTS FOR
RUNS USING HELIUM AS DILUENT

Run	X_1	X_2	Y_{He}
1	-1	-1	1.48
2	1	-1	1.97
3	-1	1	1.61
4	1	1	2.69
5	-1.633	0	1.08
6	1.633	0	2.55
7	0	-1.633	1.34
8	0	1.633	2.60
9	0	0	1.97
10	0	0	1.75

rate suggests that the rate does not depend on the SO₃ partial pressure, the mean value of which would have varied with the flow rate, for the conditions of low conversion to SO₃ used. It also indicates no interphase mass transport effects. Because both of these effects should inhibit the rate of reaction, compensation of one effect by the other can be ruled out.

Calculation of the partial pressure differences across the gas film at the catalyst surface verified the absence of interphase mass diffusion effects. Similar calculations for heat transfer showed that this process was rapid and did not disguise the rate measurements. Intraparticle mass and heat transfer calculations indicated that the reaction rates were not influenced by these factors (10). Yeramian *et al.* (2) found experimentally no difference in rates in this system using catalyst sizes of 40/60 and 20/30 mesh at 442°C. Rates measured in this study, then, are truly kinetic rates uninfluenced by macroscopic mass or heat transfer phenomena.

Empirical rather than so-called mechanistic models were used to interpret the rate measurements because the former are more adaptable to discerning effects of variables. Furthermore, a mechanistic model incorporating the diluent gas effect is not available since the source of the effect remains unknown. Mechanistic models exist indeed for SO₂ oxidation over vanadia catalysts but there is no consensus as to which is correct or even best. Testing different mechanistic models could have been undertaken but this was not the intent of the study. Furthermore, drawing mechanistic inferences from this type of activity is now regarded as futile.

The argon and helium data sets were fitted by Eqs. (1) and (2), respectively.

$$\hat{Y}_{\text{Ar}} = 2.3715 + 0.3990 x_1 + 0.3579 x_2 + 0.2452 x_1^2, \quad (1)$$

$$\hat{Y}_{\text{He}} = 1.904 + 0.3928 z_1 + 0.2128 z_2 + 0.1475 z_1 z_2, \quad (2)$$

where x_1 , x_2 , z_1 , and z_2 are the transformed variables related to the true independent variables defined in Table 1 as

$$x_1 = 1.36484 X_1 - 0.36484 X_1^3, \quad (3)$$

$$x_2 = 0.12665 X_2 + 0.87335 X_2^3, \quad (4)$$

$$z_1 = 0.91292 X_1 + 0.08708 X_1^3, \quad (5)$$

$$z_2 = 0.51244 X_2 + 0.48756 X_2^3. \quad (6)$$

Appendix 2 shows from an analysis of variance that a good fit of both Eq. (1) and (2) to their respective data sets, was obtained. The tests used pooled estimates of replication error from both helium and argon data.

Since the experiments were done in two sets, it is necessary to show that there were no trends with time in either set. Figure 1 shows the residuals ($Y - \hat{Y}$) plotted in time sequence for the argon and helium sets. No trends are evident; thus, we may conclude that any differences in rate are due to differences in the influence of the inert diluent gases.

Figure 2 shows the difference between predicted rates with argon and helium using Eqs. (1) and (2) as a function of the partial pressures of oxygen and SO₂. The experimental points are also shown. Appendix 3 shows *t* tests of the differences between these predictions taken at the same coordinates as those used experi-

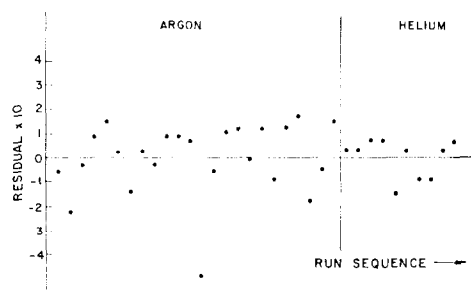


FIG. 1. Plot of overall residuals of experimental runs in sequence. Order of performance of runs: Using argon: 11, 14, 16, 10, 9, 15, 2, 13, 12, 6, 8, 23, 17, 18, 22, 20, 21, 19, 24, 4, 7, 3, 1, 5. Using helium: 3, 1, 9, 8, 10, 4, 6, 5, 2, 7. Units of residuals are those of Y .

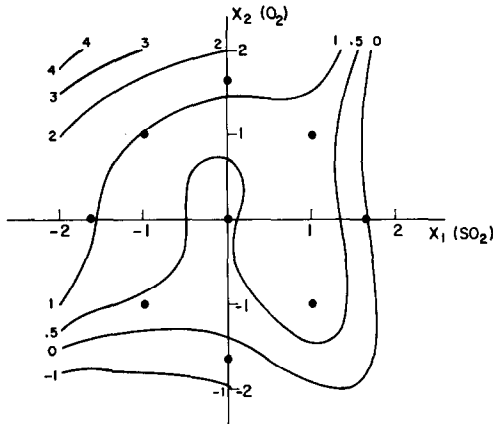


FIG. 2. Difference between rates of reaction predicted by Eq. (1) (argon) and Eq. (2) (helium) versus SO_2 partial pressure (X_1) and O_2 partial pressure (X_2). Constant difference contours are shown; (●), experimental points.

mentally. All but one point ($X_1 = 1.633$, $X_2 = 0$) show significant differences at a 95% level of confidence. Thus, a diluent gas effect is established by these data. The important finding, however, shown by the difference contours in Fig. 2 is that the diluent gas effect is composition dependent.

Figure 3 is a transformation of the data of Fig. 2, made to assist in interpreting the experimental results. The figure shows the ratio of reaction rates with argon and helium, respectively, as a function of the SO_2/O_2 mole ratio. It is evident again that the diluent gas effect is dependent on com-

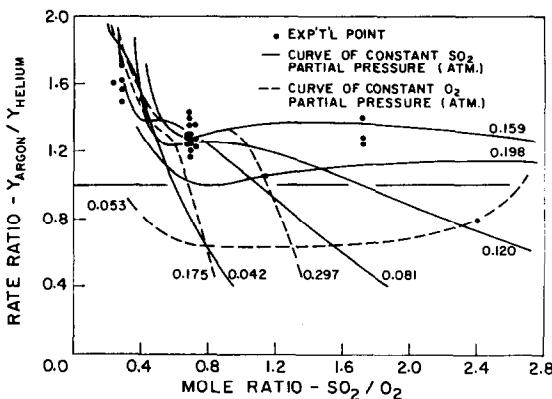


FIG. 3. Ratio of reaction rate with argon and helium vs. mole ratio SO_2/O_2 in feed.

position. At low SO_2/O_2 ratios where the mole ratio appears to be the most important variable, the diluent gas effect is pronounced. At high SO_2/O_2 ratios, the effect may vanish, depending perhaps upon the magnitudes of the individual partial pressures themselves. At low partial pressures of O_2 , the empirical models predict that the rate of reaction will be higher for helium than for argon diluent regardless of the mole ratio of SO_2/O_2 . This curve (O_2 partial pressure = 0.053 atm) is an extrapolation of a data point corresponding to a low SO_2/O_2 ratio. Recent experiments performed in our laboratory confirm that the inert gas effect disappears at high SO_2/O_2 ratios (11).

The dependence of the diluent gas effect on composition of the reactants is a new observation. It appears then for SO_2 oxidation over vanadia that whether or not a diluent gas effect will be observed depends upon the choice of reactants. If this is a general result, it may be one reason why the effect has not been reported for other catalytic systems.

The finding undercuts the collision desorption explanation for the effect offered by Baron, Manning, and Johnson (1). Their theory assumed SO_2 oxidation was controlled by desorption of SO_3 from the catalyst surface. Desorption, they claimed, occurred predominantly through collision of gas phase molecules with adsorbed SO_3 . This mechanism does not allow an effect of the SO_2/O_2 ratio. Indeed, this effect suggests the diluent gas effect is probably associated with an adsorbed phase on the catalyst surface, or, with the bulk of the catalyst phase. It is well established that the valence of vanadium in the catalyst and the ratio of the oxides to sulfate depend on the gas phase (5) under the conditions used in the experiment.

Since this work was submitted, a more detailed study of possible causes of this effect has been presented (12) in a review article.

APPENDIX 1

Transformation of Independent Variables to Form Empirical Models for Helium and Argon Runs

Preliminary fitting showed that the standard model corresponding to the composite design which was used (8) gave significant lack of fit for both helium and argon data. The addition of the cubic terms and the use of transformations of the dependent variable by the method of Box and Cox (13) were first attempted but were found still to produce significant lack of fit.

The successful models which were finally used were achieved by transforming the independent variables by a method which was at least in the spirit of that developed by Box and Tidwell (14). The simplest such transformations, being power transformations, are those that leave X_1 and X_2 unaltered if they have the values 0 or 1 (see Table 1). Values of ± 1.633 for the independent variables would however change. The best of these transformations was found for each of the helium and argon runs separately by finding to what values the ± 1.633 values should be changed so as to minimize the

sum of squared residuals. The transformation was then found which changes the ± 1.633 values to these fitted values while leaving the 0 and 1 values unchanged. The resulting transformations were those shown in Eqs. (3)–(6). Equations (1) and (2) resulted after rejecting nonsignificant terms from the full models based on the transformed independent variables.

APPENDIX 2

Statistical analyses of the data are shown in Table 4.

APPENDIX 3

The test quantities shown in Table 5 were calculated by the basic formula

$$t = (\hat{Y}_{Ar} - \hat{Y}_{He}) (\text{Estimated Var } \hat{Y}_{Ar} + \text{Estimated Var } \hat{Y}_{He})^{-1/2}$$

which expresses the difference in predictions obtained from Eqs. (1) and (2) as a multiple of the estimated standard deviation of the difference. The estimated variances of the predictions \hat{Y}_{Ar} and \hat{Y}_{He} were obtained through Eqs. (1) and (2) by the use of the estimated variances and covariances among the estimated coefficients. These latter variances were based

TABLE 4
ANALYSIS OF VARIANCE

Source	Sum of squares			Degrass of freedom			Mean square		
	Argon	Helium	Total	Argon	Helium	Total	Argon	Helium	Total
Regression	164.367313	39.010284	203.377597	6	6	12			
Replicates	0.152950	0.024200	0.177150	9	1	10	0.01699	0.02420	0.01772
Lack of fit	0.365137	0.03216	0.398053	9	3	12	0.04057	0.01097	0.03317
Total	164.885400	39.067400	203.952800	24	10	34			

<i>F</i> tests	Ratio	Numerical ratio	Tabulated <i>F</i> value
Consistency of errors	Mean square helium replicates/ mean square argon replicates =	1.424	$F_{95}\left(\frac{1}{9}\right) = 5.12$
Lack of fit, argon model	Mean square argon lack of fit/ mean square total replicates =	2.290	$F_{95}\left(\frac{9}{10}\right) = 3.02$
Lack of fit, helium model	Mean square helium lack of fit/ mean square total replicates =	.619	$F_{95}\left(\frac{3}{10}\right) = 3.71$
Lack of fit, overall	Mean square total lack of fit/ mean square total replicates =	1.872	$F_{95}\left(\frac{12}{10}\right) = 2.91$

TABLE 5
t TESTS ON DIFFERENCE BETWEEN PREDICTIONS

X_1	X_2	<i>t</i> Value
-1	-1	3.058
1	-1	5.320
-1	1	7.383
1	1	5.286
-1.633	0	9.356
1.633	0	(0.529) ^a
0	-1.633	-2.266
0	1.633	8.535
0	0	6.944

^a Not significant.

on our error estimate from replicates of 0.17715, which had 10 *df*.

The comparison value for the *t* statistic for 95% confidence at 10 *df* is 2.228. Test quantities (*t* values) greater in absolute value than this are significant.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial assistance of the National Research Council of Canada in the form of a research grant (to R. R. Hudgins) and a research fellowship (to W. G. Rhodey).

Catalyst was provided by Cyanamid of Canada, Limited.

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