COMMUNICATIONS TO THE EDITOR

The Interpretation of Initial Rate Data with the Use of Hougen-Watson Models

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Mathur and Thodos (*1*) illustrated the use of initial reaction rates in the specification of an adequate Hougen-Watson model (*2, 3*) for the oxidation of sulfur dioxide. The general approach advocated by these authors and others (*4*) is to take initial rate data as a function of total pressure. The shape of this profile, then, allows the elimination of certain models incapable of describing the reaction. (An equivalent procedure is to linearize the model by an algebraic rearrangement, to plot the data in this linearized form, and to examine the data for deviations from linearity.) The three characteristics of the shape of the initial rate profile which are generally thought to be useful in this model elimination are an absolute maximum in the initial rate data, a horizontal asymptote of the data, or a tendency for the initial rate data to increase continually with increasing pressure. After the elimination of those models which are not capable of describing the observed characteristics of the rate data, the remaining models are linearized by algebraic manipulation and fitted to the data by linear least squares. The signs of the parameter estimates thus obtained are used for eliminating additional models on physical grounds. The use of initial rate profiles is generally an effective method of eliminating obviously inadequate reaction rate models. Some disadvantages of the use only of these profiles and the signs of the parameter estimates have been discussed elsewhere (*5*).

The purpose of this communication is to present an additional characteristic of the initial rate profiles useful for eliminating inadequate models. Also, a danger of implicit extrapolation of initial rate data in the data analysis will be discussed. This will be done through the above-mentioned data on the oxidation of sulfur dioxide.

TABLE 1. RIVAL MODELS FOR SULFUR DIOXIDE OXIDATION

Model No. (*1*)	Model
5*a* and 7*a*	$r_0 = \dfrac{a\pi}{(1 + b\pi)^2}$
6*a*	$r_0 = \dfrac{a\pi}{1 + b\pi}$
6*b* and 7*b*	$r_0 = \dfrac{a\pi^{3/2}}{1 + b\pi + c\pi^{3/2}}$
7*c*	$r_0 = \dfrac{a\pi^{3/2}}{(1 + b\pi)^2}$

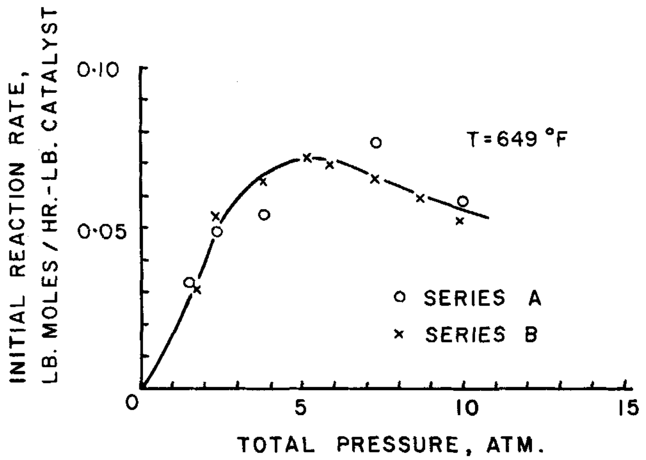

Fig. 1. Initial rate profile for 649°F. data.

At one stage of the Mathur and Thodos analysis of the sulfur dioxide oxidation data (*1*), six rival models remained; these are listed in Table 1. Mathur and Thodos arrived at these six models using the initial rate data and the signs of the linear regression coefficients. The initial rate data are plotted in Figures 1, 2, and 3, as taken from the original article. Noting that models 5*a*, 7*a*, and 7*c* exhibit a maximum in the initial rate-pressure profile, while models 6*a*, 6*b*, and 7*b* have a horizontal high-pressure asymptote, Mathur and Thodos felt that the initial rate data suggested a shift in mechanism with temperature. On the basis of the physically most realistic shift in mechanism, they chose model 7*c* for the 649° and 701°F. data and model 7*b* for the 752°F. data. Using the data alone, however, they could not reduce the number of possible models to less than two for any of the three temperature levels. We shall show how only one model of those in Table 1 is compatible with the 701°F. data and that this model cannot be rejected by the data of the other two temperature levels (649° and 752°F.).

In further discriminating among six such rival models, the maximum in the initial rate data of Figures 1 and 2 is often used. Note from Table 2 that the first derivatives of models 6*a*, 6*b*, and 7*b* are not zero for nonzero, positive, finite-pressure levels. Thus, since these models cannot exhibit a maximum in an initial rate-total pressure correlation, they may be eliminated from further consideration for the 649° and 701°F. data. For these two data sets, then, only models 5*a*, 7*a*, and 7*c* could be appropriate.

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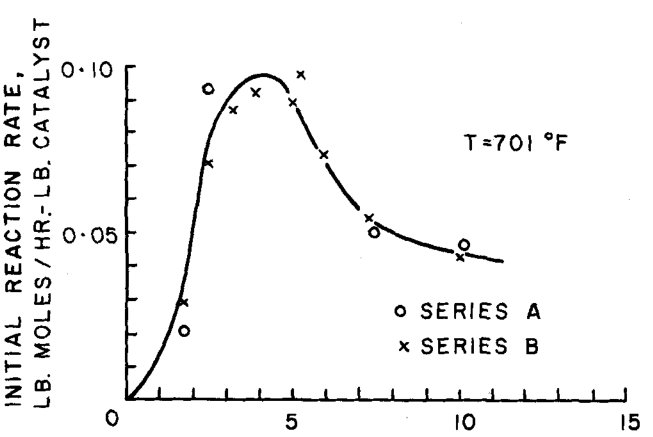

Fig. 2. Initial rate profile for 701°F. data.

An additional characteristic of these data of value for model discrimination, which is commonly not used, is the low-pressure inflection point. In particular, the inflection point at low pressures in Figure 2 demands that an adequate reaction rate model must also *exhibit this inflection* point. Let us examine the three remaining rival models at the 701°F. level (5*a*, 7*a*, 7*c*) to determine their ability to exhibit such an inflection point. For the inflection point to exist for these models, there must be a low-pressure maximum in the first derivative of the model with respect to pressure. That is, the second derivative with respect to pressure *of the initial rate model must be zero for* pressures between zero and the pressure at which the maximum in r_0 vs. π occurs. The points at which r_0, $dr_0/d\pi$, and $d^2r_0/d\pi^2$ are zero for these three models are shown in Table 2. It can thus be seen that only model 7*c* fulfills this requirement; it is the only model of Table 1 that can represent the 701°F. data. As shown by Figure 1 the 649°F. data also seem to exhibit this inflection point, although the scarcity of low-pressure data prevents an unqualified statement as to its presence. The dashed line of Figure 3, a possible extrapolated behavior of the data at low pressures, suggests that the 752°F. data also have not been taken at sufficiently low pressures to determine if an inflection point exists. Hence, of the models of Table 1, only model 7*c* can apply to the 701°F. data. For the 649°F. data, on the other hand, any of models 5*a*, 7*a*, or 7*c* could apply, due to the lack of data near the low-pressure inflection point.

The data at 752°F. reveal nothing about the existence of an inflection point at low pressures, as mentioned earlier. However, it should be noticed that a maximum in the initial rate-pressure profile *could* exist if data were present at higher pressures. A fit of model 7*c* to these 752°F. data, in fact, provides the solid line of Figure 4. This fitted curve was drawn by using the constant mole fractions shown on the figure. *Since the experimental data* were taken at slightly different mole fractions, scatter of the data about the fitted line exists in this figure in addition to that due to experimental error. Model 7*c* was fitted to the 752°F. data by nonlinear least squares with a residual sum of squares of 13.7 × 10^{-4}, comparing well with the 7.6 × 10^{-4} residual sum of squares for model 7*b* (the model suggested by Mathur and Thodos). The ratio of these sums of squares is 1.8, while the appropriate *F* statistic is 2.1 at the 95% confidence level. Hence, lacking an independent estimate of experimental error, these 752°F. data cannot be said to reject model 7*c*, even though models 5*a*, 6*a*, 6*b*, 7*a*, and 7*b* also have not been rejected by the data.

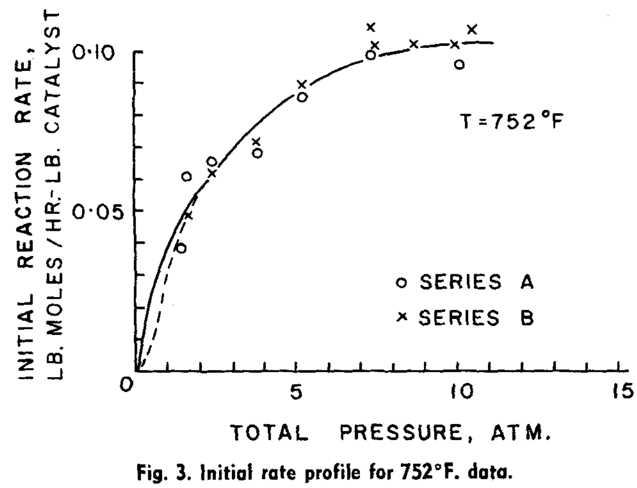

Fig. 3. Initial rate profile for 752°F. data.

TABLE 2. ZERO POINTS FOR RIVAL MODELS

Model	Pressures at which		
	$r_0 = 0$	$dr_0/d\pi = 0$	$d^2r_0/d\pi^2 = 0$
5*a* and 7*a*	0, ∞	$1/b$, ∞	$2/b$, ∞
6*a*	0	∞	$-1/b$, ∞
6*b* and 7*b*	0	0, ∞	x,* ∞
7*c*	0, ∞	0, $3/b$, ∞	$\frac{0.172}{b}, \frac{5.828}{b}, \infty$

* $\pi = x$ is the real, finite-positive solution to the equation $3 - 6b\pi - 15c\pi^{3/2} - b^2\pi^2 - 3bc\pi^{5/2} = 0$.

In summary, of the models of Table 1, only model 7*c* has not been rejected *by the data* at 701°F., and it is one of several models which is as yet unrejected by the data at the other two temperature levels. Although the data do not preclude the hypothesis of a mechanism shift at *each* of the three temperature levels, a simpler and equally reasonable conclusion is that model 7*c* describes all of the available data presented for the oxidation of sulfur dioxide as well as any of the models of Table 1. Thus, this model was fitted to the data of all of the temperature levels simultaneously by nonlinear least squares. The parameter estimates in the temperature-dependent model 7*c*

$$r_0 = \frac{\exp(-E/RT + \Delta S_1/R)\exp(-\Delta H/RT + \Delta S_2/R)p_{SO_2}p_{O_2}^{1/2}}{[1 + \exp(-\Delta H/RT + \Delta S_2/R)p_{SO_2}]^2} \tag{1}$$

are shown in Table 3. The signs of *E*, ΔH, and ΔS_2 are in accordance with the usual predictions of heterogeneous kinetic theory for adsorption without dissociation (*6*). The fit of all three temperatures simultaneously by Equation (1) produced an average deviation of the predicted from the experimental rates of 19%. This can be compared to the average deviation of the predicted from the experimental rates of 8.3% obtained in the original work (*1*), using isothermal data and two models (7*b* and 7*c*). Since a single model was, in our case, required to fit the data of all three temperatures simultaneously, this difference in the average deviation is as expected. The contributions of the deviation of each temperature level to the 19% average were 16, 33, and 10%, which are compatible with the previously reported (*1*) *isothermal* values of 4.2, 20.1,

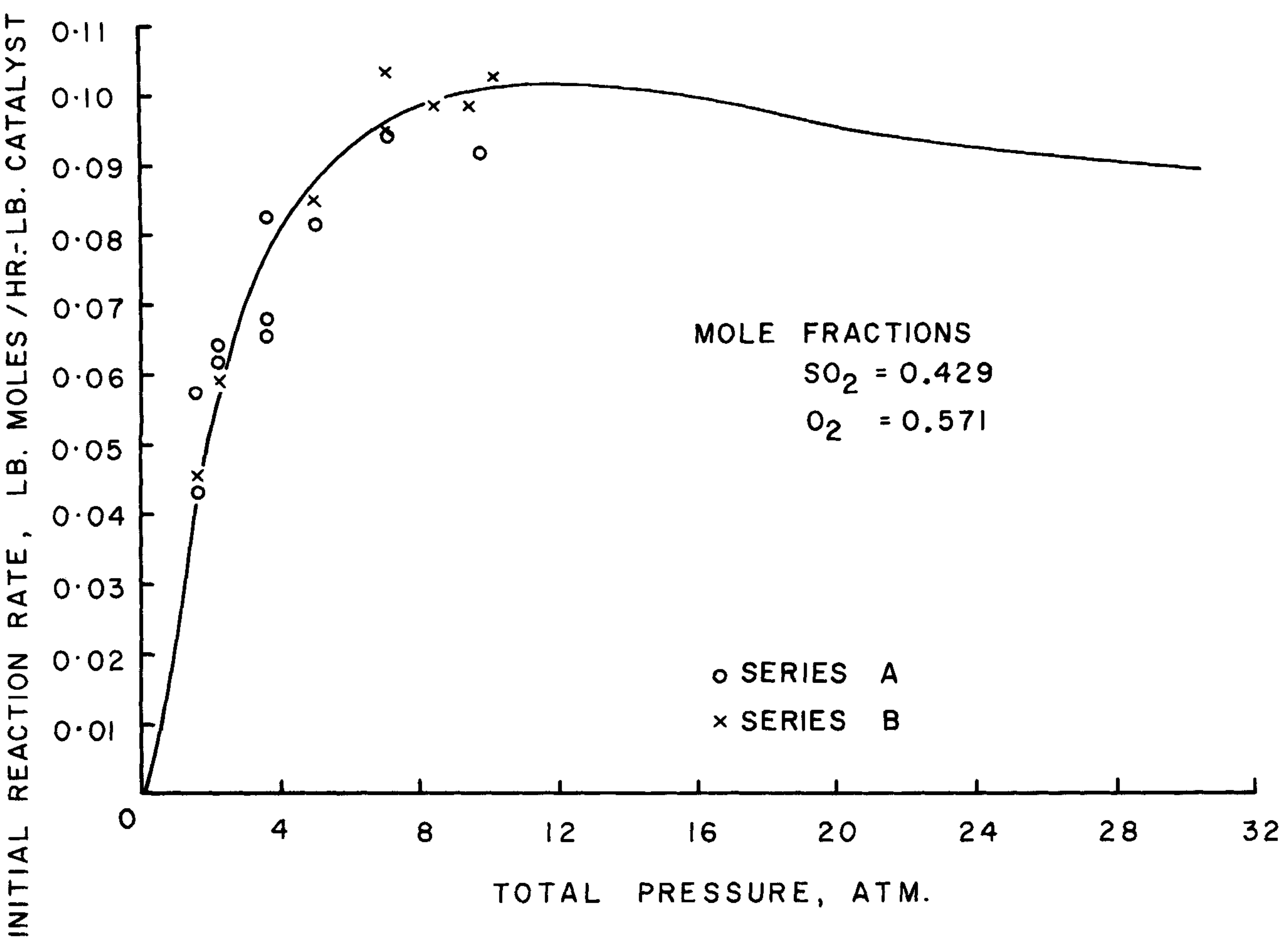

Fig. 4. Nonlinear least squares fit of all isothermal 752°F. data for model 7c.

and 1.0% for 649°, 701°, and 752°F., respectively. The largest contributions to the deviation at 701°F. were at extremely low and extremely high pressures. This percent deviation is of the same order of magnitude as that reported for other heterogeneous kinetic studies (*7*).

It can be seen that additional progress can be made toward the specification of an adequate describing model for these data by using the inflection point of the initial rate data as well as their maximum with pressure. Also, Figure 4 illustrates the danger of implicitly extrapolating the 752°F. data by assuming that it could not exhibit a maximum; in fact model 7c fits these data better than it does that of the two lower temperature levels. We have found a single model describing all of the data reasonably well, with parameter estimates fully compatible with our knowledge of adsorption theory without dissociation of the adsorbed species. We have not, however, been able to show that the model of Equation (1) is better than many of the other models of Table 1 for 649° and 752°F. by the kinetic data alone. The problem here is due to the limited ranges of the variables used (*5*, *8*), as is often the case. *If* experimental conditions will allow a wider range of pressure, perhaps even with slight equipment modifications, sequential experimental design procedures (*8*) will direct the experimenter's attention to regions of operation allowing an effective and efficient discrimination between the several models while the experimentation is in progress. In this case, such experimental design procedures would perhaps have suggested operation at lower pressures to define the presence or absence of the inflection point and higher pressures to define the presence or absence of the maximum in the higher temperature data.

TABLE 3. PARAMETER ESTIMATES FOR MODEL 7c AND EQUATION (1)

Parameter	Magnitude*
E	2,510 ± 2,980 cal./g.-mole
ΔS_1	0.681 ± 4.35 cal./(g.-mole)(°K.)
ΔH	−6,460 ± 7,410 cal./g.-mole
ΔS_2	−10.18 ± 11.13 cal./(g.-mole)(°K.)

* The numbers following the ± signs approximate the 95% confidence interval for the parameter estimates.

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NOTATION

a = collection of kinetic terms and mole fractions for the rate equations of Table 1
b = collection of adsorption constants and mole fractions for the rate equations of Table 1
E = energy of activation, cal./g.-mole

ΔH = enthalpy change, cal./g.-mole
p_{SO_2} = partial pressure of sulfur dioxide, atm.
p_{O_2} = partial pressure of oxygen, atm.
R = universal gas constant, 1.98 cal./(g.-mole) (°K.)
r_0 = initial reaction rate, lb.-moles sulfur dioxide/(hr.) (lb. catalyst)
ΔS = entropy change, cal./(g.-mole) (°K.)
T = absolute temperature, °K.
π = total pressure, atm.

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Power Consumption in the Agitation of Solid-Liquid Suspensions

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This paper discusses experiments carried out to provide data describing power consumption characteristics in agitated vessels containing solid-liquid, two-phase systems. These experiments involved several slurry systems, and the data were treated by modifying the properties density and viscosity which appear in the Reynolds and Power numbers. Liquid-liquid and vapor-liquid experiments yielding power consumption data have been reported (*7*, *2*, *5*, *8*); the data for single-phase liquids have been recently thoroughly summarized by Bates et al. (*1*).

When the suspension of solids is reasonably stable, powerful methods for power requirement determinations have been suggested based on concepts of non-Newtonian fluid systems (*6*). When the suspension of solids is not stable, that is, the solids settle freely, the work of Weisman and Efferding and others cited there (*12*) discuss criteria for obtaining complete suspension of the solids. This work is summarized by Perry (*10*).

The following discussion describes work carried out in which power measurements were made for agitated vessels in which the solids suspended do not generally form stable suspensions. In all runs the suspension was such that no particles remained stationary on the tank bottom. This is the criterion for complete suspension used by Hirsekorn and Miller (*3*), and Weisman and Efferding agreed with this criterion, at least to the level of the slurry-liquid interface. The interior of the vessel was completely submerged so that no air-liquid interface and no vortex problems were present. In all runs the slurry existed throughout the entire interior. Thus, the objective here is an investigation into the power consumption characteristics of uniformly distributed particles in an agitated vessel. In the practical situation, this occurs when the primary objective of the operation is some transport process such as solids dissolution, heat transfer in a particulate two-phase system, or crystallization.

APPARATUS

The agitation vessel used for most runs was a Pyrex battery-type jar, 21.4 cm. I.D., which was immersed partially in water contained in a larger diameter battery jar for temperature control. This entire assembly was placed on a Plexiglas sheet over an inclined mirror so that particles of the solids being suspended could be carefully observed at the bottom of the vessel. Four 0.1-diameter radial baffles were employed.

The volume of fluid agitated in this vessel was maintained constant by sealing a fixed plate 19.5 cm. from the bottom. Holes were cut into this plate to allow the agitator shaft to pass through, filling and draining of the system, and thermometer insertion. A small chimney about the center hole and shaft permitted air to escape before making a run and also provided for an extra head of liquid which helped avoid vortex formation due to the leakage of air about the shaft. The plate was sealed against the glass walls of the vessel and the baffles; the thermometer and solids feed holes were tightly stoppered. About 1 in. of distilled water was maintained above this horizontal partition to avoid air entrainment. Only insignificant amounts of solids of any size were found to permeate this upper region.