TABLE 1. WALL REGION MASS TRANSFER DATA

Investigator	Method	Average a
Shaw and Hanratty	Ferricyanide reduction	0.063
Hubbard and Lightfoot	Ferricyanide reduction	0.055
Mizushina et al.	Ferricyanide reduction	0.062
Lin et al.	Electrochemical	0.067
Meyerink and Friedlander	Wall solution	0.070
Harriott and Hamilton	Wall solution	0.078

of electrochemical reactions to obtain wall region mass transfer data. Table 1 summarizes these data to show the coefficient for the equation

$$k^+_{EW} = a\, N_{Sc}^{-2/3} \tag{3}$$

The Meyerink and Friedlander (1962) data reported in the table are for a benzoic acid pipe. The Shaw and Hanratty data are the corrected data reported by Son and Hanratty (1967). Thus Table 1 indicates that $a \approx 0.065$ is more consistent with these data than the value of $a = 0.0816$ used in the prior paper.

NOTATION

C_p = specific heat
f = Fanning friction factor
h = heat transfer coefficient
k = mass transfer coefficient
N_{Sc} = Schmidt number
U = mean velocity

Greek Letters

ρ = fluid density

Subscripts

EC = eddy diffusion, core
EW = eddy diffusion, wall

LITERATURE CITED

Harriott, P., and R. M. Hamilton, "Solid-Liquid Mass Transfer in Turbulent Pipe Flow," *Chem. Eng. Sci.*, **20**, 1073 (1965).

Hubbard, D. W., and E. N. Lightfoot, "Correlation of Heat and Mass Transfer Data for High Schmidt and Reynolds Numbers," *Ind. Eng. Chem. Fundamentals*, **5**, 370 (1966).

Hughmark, G. A., "Heat and Mass Transfer for Turbulent Pipe Flow," *AIChE J.*, **17**, 902 (1971).

Lin, C. S., et al., "Diffusion Controlled Electrode Reactions," *Ind. Eng. Chem.*, 43, 2136 (1951).

Meyerink, E. S. C., and S. K. Friedlander, "Diffusion and Diffusion Controlled Reactions in Fully Developed Turbulent Pipe Flow," *Chem. Eng. Sci.*, **17**, 121 (1962).

Mizushina, T., et al., "Turbulent Heat and Mass Transfer between Wall and Fluid streams of Large Prandtl and Schmidt Numbers," *Intern. J. Heat Mass Transfer.*, **14**, 1705 (1971).

Shaw, P. V., and T. J. Hanratty, "Fluctuations in the Local Rate of Turbulent Mass Transfer to a Pipe Wall," AIChE J., **10**, 475 (1964).

Son, J. E., and T. J. Hanratty, "Limiting Relation for the Eddy Diffusivity Close to a Wall," *ibid.*, **13**, 689 (1967).

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Parameter Estimation from Transient Rate Data

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The results of transient experiments on the decomposition of nitrous oxide over nickel oxide have been reported by Yang et al. (1972), and details of gradientless catalytic reactor which was used are also available (Bennett et al., 1972). In this work a carrier gas of argon through the reactor was suddenly replaced by various mixtures of argon and nitrous oxide at the same flow rate, pressure, and temperature. The response of the well-mixed reactor to these signals was obtained by an on-line mass spectrometer as the composition changed to a new steady state. Mass and heat transfer falsification effects were absent (Bennett et al., 1972; Yang et al., 1972).

The ordinary differential equations and the algebraic constraints which describe the transient reacting system have been given by Bennett (1967), and the latest paper (Yang et al., 1972) gives the results of a search for the parameter in a sequence of steps which describes the N_2O reaction. In these previous publications no details of the method of parameter estimation were given.

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In the following we present the procedures used in estimating the parameters and the sequence of steps for the nitrous oxide decomposition. The operation of the gradientless reactor used in this work enables the concentrations of adsorbed species to be calculated at steady state reaction conditions. This allows simplification of a proposed sequence of steps when a particular surface specie is experimentally determined not to be present. The calculated surface concentrations also yield accurate initial parameter estimates which makes the computer optimization of parameters much more efficient.

NUMERICAL TECHNIQUES

The numerical integration of the ordinary differential equations utilized the fourth-order Runge-Kutta method. A fixed integration interval of 0.4 sec was found to be adequate for all of the transient runs.

An objective function was necessary to measure the degree to which the experimental transient concentrations are described by proposed models. The following form was used:

$$\text{O.F.} = \sum_{i=1}^{M} \sum_{j=1}^{N} [(\underline{C}_{ij} - C_{ij})/\underline{C}_{ij}]^2 \qquad (1)$$

This objective function weighted individual gas phase compositions at each time interval in an equivalent manner. The total objective function was the sum of Equation (1) for the various transient runs. The error variances for the different gases were assumed here to be proportional to the magnitude of the particular concentration. A regular least squares objective function would have favored the steady state results and thus would have greatly downgraded the valuable information contained in the transient concentrations.

Minimization of the objective function was accomplished using a modified gradient procedure. The length along the gradient after an initial first step was determined from the dot product of the unit vectors of the present and previous successful gradients using the form suggested by Marquardt (1959). This effectively increased the step size as the two gradient vectors became parallel and decreased the step size as they became perpendicular. Unsuccessful steps along the gradient were decreased by one-fourth and the process repeated. Brandon (1969) has given details of this method complete with the computer program listing.

CONCENTRATIONS OF ADSORBED SPECIES

One of the attractive features of the transient experimental technique is that the concentrations of adsorbed species under steady state reaction conditions can be obtained by material balances on the reactor throughout the transient period. This procedure is illustrated for calculating $\overline{C}_{O\text{-}S}$ and $\overline{C}_{N_2O\text{-}S}$ for the three-step sequence defined by Equations (2), (3), and (4).

$$N_2O + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O\text{-}S \qquad (X2) \qquad \text{Step 1} \qquad (2)$$

$$N_2O\text{-}S \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} N_2 + O\text{-}S \qquad (X2) \qquad \text{Step 2} \qquad (3)$$

$$2O\text{-}S \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 2S + O_2 \qquad \text{Step 3} \qquad (4)$$

Since there were no reaction products in the reactor feed, the differential mass balances (Bennett, 1967) for this system may be rearranged as follows:

$$r_1 = \frac{1}{2}\left(-\frac{dC_{N_2O}}{dt} + \frac{q_f}{V} C_{N_2Of} - \frac{q}{V} C_{N_2O}\right) \qquad (5)$$

$$r_2 = \frac{1}{2}\left(\frac{dC_{N_2O}}{dt} + \frac{q}{V} C_{N_2}\right) \qquad (6)$$

$$r_3 = \frac{dC_{O_2}}{dt} + \frac{q}{V} C_{O_2} \qquad (7)$$

Substitution of Equations (6) and (7) into the differential equation for adsorbed oxygen gives

$$\frac{dC_{O\text{-}S}}{dt} = \frac{d(C_{N_2} - 2C_{O_2})}{dt} + \frac{q}{V}(C_{N_2} - 2C_{O_2}) \qquad (8)$$

where q can be obtained from

$$q = q_f + V\, C_T^{-1} \sum_{j=1}^{N} \sum_{i=1}^{E} Z_{ij}\, r_i = q_f + VC_T^{-1}(-2r_1 + 2r_2 + r_3) \qquad (9)$$

This equation allows the reactor exit flow rate to be calculated as a function of the elementary reaction rates during the transient period. The rates from Equations (5) to (7) are inserted in Equation (9), and Equation (9) is substituted into Equation (8) to yield

$$\frac{dC_{O\text{-}S}}{dt} = \frac{d(C_{N_2} - 2C_{O_2})}{dt} + \frac{q_f}{V}\frac{C_{Arf}}{C_{Ar}}(C_{N_2} - 2C_{O_2}) - \frac{1}{C_{Ar}}\frac{dC_{Ar}}{dt}(C_{N_2} - 2C_{O_2}) \qquad (10)$$

This equation can be integrated from $t = 0$ to $t = t_s$ where t_s is the time to reach steady state, where

$$C_{N_2} = 2C_{O_2} \qquad (11)$$

Integration of Equation (10) gives an expression for the adsorbed atomic oxygen.

$$\overline{C}_{O\text{-}S} = \frac{q_f}{V}\int_0^{t_s} \frac{C_{Arf}}{V}(C_{N_2} - 2C_{O_2})\, dt - \int_{C_{Ar_0}}^{\overline{C}_{Ar}} \left(\frac{C_{N_2} - 2C_{O_2}}{C_{Ar}}\right) \frac{dC_{Ar}}{dt}\, dt \qquad (12)$$

A similar procedure yields an equation for the adsorbed nitrous oxide.

$$\overline{C}_{N_2O\text{-}S} = \frac{q_f}{V}\int_0^{t_s} \left(C_{N_2Of} - \frac{C_{Arf}}{C_{Ar}}(C_{N_2O} + C_{N_2})\right) dt + \int_{C_{Ar_0}}^{\overline{C}_{Ar}} \frac{C_{N_2O} + C_{N_2}}{C_{Ar}} \frac{dC_{Ar}}{dt}\, dt - (\overline{C}_{N_2O} + \overline{C}_{N_2}) \qquad (13)$$

Application of Equations (12) and (13) requires that the term $(C_{N_2} - 2C_{O_2})$ should approach zero or stoichiometric at steady state. Thus the concentration transients of nitrogen, oxygen, and argon were multiplied by constants based on the conversion of nitrous oxide to compensate for the experimental errors at steady state.

Table 1. Oxygen Adsorption from Transient Reaction Measurements

Run no.	Adsorbed oxygen × 10^7 (gmol/g)	Nitrous oxide × 10^5 (gmol/cm^3)	Oxygen × 10^6 (gmol/cm^3)	Temperature, °C
1	7.8	0.179	0.171	332
2	8.8	0.337	0.109	332
3	8.1	0.533	0.227	332
4	14.4	0.718	0.301	332
5	10.2	0.902	0.354	332
6	14.3	1.068	0.365	332
7	13.0	1.259	0.381	332
8	13.6	1.402	0.398	332
9	13.8	0.259	0.292	352
10	20.0	0.423	0.425	352
11	18.2	0.556	0.533	352
12	24.1	0.696	0.646	352
13	20.9	0.861	0.721	352
14	23.4	1.014	0.766	352
15	22.7	1.144	0.858	352
16	12.8	0.148	0.230	352
17	15.4	0.134	0.353	372
18	22.2	0.256	0.579	372
19	19.7	0.370	0.716	372
20	22.9	0.528	0.942	372
21	24.3	0.793	1.126	372
22	23.2	0.788	1.465	372

The calculated results are presented in Table 1 for the adsorbed oxygen. The amount of adsorbed nitrous oxide was so small that it could not be accurately calculated. The amount of adsorbed oxygen corresponds to less than a 1% monolayer on the nickel oxide. We have commented on the probable nature of the adsorbed oxygen and its temperature dependence (Yang et al., 1972). The values in Table 1 do not depend on the forms of the rate equations for the steps but are the result of a mass balance. The quantity of oxygen adsorbed during reaction at steady state may be different from that in equilibrium with the reported gas-phase oxygen concentration.

MODEL SIMPLIFICATION

The lack of any adsorbed nitrous oxide during the reaction simplifies the proposed surface processes to the following two sequences (Yang, 1971):

Sequence I $\quad N_2O + S \rightarrow N_2 + O\text{-}S \qquad (14)$

$2\,O\text{-}S \rightleftarrows O_2 + 2S \qquad (15)$

Sequence II $\quad N_2O + S \rightarrow N_2 + O\text{-}S \qquad (16)$

$N_2O + O\text{-}S \rightleftarrows N_2 + O_2 + S \qquad (17)$

The remaining discussion will be limited to the evaluation of these two sequences with the transient data. For the above sequences where the second step is reversible, designated Sequence I-R and Sequence II-R, this is accomplished by determining the four parameters k_1, k_2, k_{-2}, and C_{S_0} which minimize the objective function. The special cases where the second step is in quasi-equilibrium, Sequence I-E and Sequence II-E need only three parameters, as k_2 and k_{-2} are replaced by K_2.

For Sequence I-R, the following rate equations apply:

$$r_1 = k_1\, C_{N_2O}\, C_S \tag{18}$$

$$r_2 = \frac{k_2\, C_{O\text{-}S}^2}{C_{S_0}} - k_{-2}\frac{C_{O_2}\, C_S^2}{C_{S_0}} \tag{19}$$

The form of Equation (19) follows Boudart (1968) and the parameters k_2 and k_{-2} contain the constant factors 1/2 Z when Z is the number of nearest neighbors adjacent to an active site. Similar equations apply to Sequence II-R. For Sequences I-E and 2-E, with step one rate determining, the values of r_2 in the model are obtained by a mass balance; since this step is at quasi-equilibrium, Equation (19) reduces to the equilibrium relation

$$\frac{k_2}{k_{-2}} = K_2 = \frac{C_S^2\, C_{O_2}}{C_{O\text{-}S}^2} \tag{20}$$

and cannot be used to calculate r_2.

ISOTHERMAL OPTIMIZATIONS

The transient experimental data were first examined with respect to Sequences I and II at each of the three temperatures. These results are summarized in Table 2. Note that there are consistent trends with temperature for the rate constants in each model and that the concentration of total sites increases with temperature.

Consideration of the objective function values indicates that the best model is given by Sequence I-R where the second step is reversible but not at equilibrium. Both models of Sequence I represent the data almost equally well at 372°C. This is because the quasi-equilibrium of step 2 for Sequence I is nearly attained at the highest temperature. Sequence II-E for step 2 at equilibrium was not considered because the objective function could at best approach that of the four parameter Sequence II-R model.

Sequences I-E, II-R and II-E were eliminated from further modeling considerations because of their inability to represent the transient data at the lower temperatures.

Good initial parameter estimates are necessary for the computer optimization to avoid a possible convergence to a false minimum. In this work, the estimates were obtained by using the previously calculated adsorbed oxygen concentrations. The first transient run at 332°C was used to obtain the parameter estimates. The steady state reaction rate for Sequence I-R is related to the steady state concentrations and the parameters as follows:

$$\bar{r} = k_1\, \overline{C}_{N_2O}\, \overline{C}_S = k_2\frac{\overline{C}_{O\text{-}S}^2}{C_{S_0}} - k_{-2}\frac{\overline{C}_{O_2}\, \overline{C}_S^2}{C_{S_0}} \tag{21}$$

Table 2. Isothermal Parameter Values

Sequence I-R	332°C	352°C	372°C
$C_{S_0} \times 10^6$ gmol/g	1.58	3.26	4.64
$k_1 \times 10^{-4}$ cm^3/gmol · sec	1.13	1.29	1.78
$k_2 \times 10^1$ sec^{-1}	2.15	5.61	13.0
$k_{-2} \times 10^{-5}$ cm^3/gmol · sec	4.75	9.40	10.7
O.F.	7.30	6.74	2.55
Sequence I-E			
$C_{S_0} \times 10^6$ gmol/g	1.95	3.59	4.75
$k_1 \times 10^{-4}$ cm^3/gmol · sec	.812	1.12	1.74
$K_2 \times 10^{+7}$ gmol/cm^3	3.34	5.78	9.90
O.F.	11.2	8.2	2.6
Sequence II-R			
$C_{S_0} \times 10^6$ gmol/g	2.19	3.44	4.36
$k_1 \times 10^{-4}$ cm^3/gmol · sec	1.28	2.06	3.08
$k_2 \times 10^{-4}$ cm^3/gmol · sec	2.35	2.95	4.43
$k_{-2} \times 10^{-11}$ cm^6/gmol^2 · sec	15.2	5.04	1.98
O.F.	14.65	9.59	5.15

An assumption that the forward rate of step 2 is twice that of the reverse rate of step 2 yields the following equations for the estimates:

$$k_1 \simeq \bar{r}/[C_{N_2O}(C_{S_0} - \overline{C}_{O\text{-}S})] \tag{22}$$

$$k_2 \simeq 2\,\bar{r}\,C_{S_0}/\overline{C}^2_{O\text{-}S} \tag{23}$$

$$k_{-2} \simeq k_2\,\overline{C}_{O\text{-}S}{}^2/[2\overline{C}_{O_2}\,(C_{S_0} - \overline{C}_{O\text{-}S})^2]$$

These estimates involve the steady state concentrations for the first transient run, the $\overline{C}_{O\text{-}S}$ which has been calculated, and C_{S_0} which was obtained from a one parameter search on this transient run. Converged values of the parameters at 332°C shown in Table 2 were used as the initial estimates for the next higher temperature. Initial estimates for the other sequences were obtained in a similar manner.

TEMPERATURE DEPENDENT OPTIMIZATION

The parameters of Table 2 for Sequence I-R are shown as points in the Arrhenius plot of Figure 1. An optimization which included all 22 transient runs produced the final Arrhenius expressions for the parameters given in Table 3. These are plotted as the straight lines in Figure 1. Initial estimates for this final optimization came from a weighted normalized-sum-of-the-squares regression on the individual parameters with temperature. The weighting factors were the corresponding objective function at each temperature. The parameter values from the final optimization yield a deviation between the computed concentration-time transients and the experimental transients of approximately 5%.

Table 3. Temperature Dependency of Parameters for Sequence I-R

$k_1 = 7.83 \times 10^6 \exp(-7\,887/RT)$ cm³/gmol · sec
$k_2 = 4.40 \times 10^{11} \exp(-34\,059/RT)$ sec^{-1}
$\kappa_{-2} = 7.24 \times 10^{11} \exp(-17\,037/RT)$ cm³/gmol · sec
$C_{S_0} = 68.9 \exp(-21\,082/RT)$ gmol/g
O.F. = 18.5

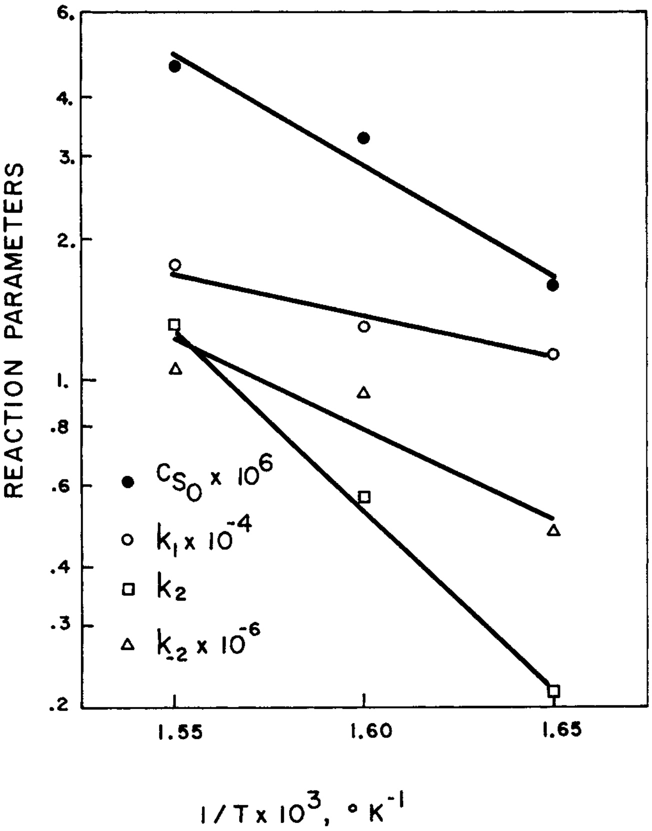

Fig. 1. Parameters for Sequence I-R.

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NOTATION

Ar = argon
C_{Ar0} = initial concentration of argon in reactor, gmol/cm³
C_{ij} = measured gas concentration at time t_i
$\underline{C}_{ij}$ = calculated gas concentration at time t_i
C_j = concentration of jth species, gmol/cm³
$\overline{C}_j$ = steady state concentration of jth species, gmol/cm³
C_{jf} = concentration of jth species in reactor inlet, gmol/cm³
C_{S_0} = total concentration of catalyst sites, gmol/g
C_T = total concentration, gmol/cm³
E = number of elementary steps
k_i = forward rate constant for ith step
k_{-i} = reverse rate constant for ith step
K = overall thermodynamic equilibrium constant
K_i = equilibrium constant for ith step
N = number of gaseous species
M = number of equal time intervals
O.F. = objective function
P = reactor pressure
q = outlet flow rate from reactor, cm³/sec
q_f = inlet flow rate to reactor, cm³/sec
$\bar{q}$ = outlet flow from reactor at steady state, cm³/sec
r_i = elementary rate of ith step, gmol/g min
$\bar{r}$ = steady state reaction rate, gmol/g min
R = gas constant
S = catalyst surface site
t = time, sec
T = reactor temperature
V = total gas volume in the reactor, cm³
Z_{ij} = stoichiometric coefficient of C_j in ith step

LITERATURE CITED

Bennett, C. O., "A Dynamic Method for the Study of Heterogeneous Catalysis," *AIChE J.*, 13, 890 (1967).
Bennett, C. O., M. B. Cutlip, and C. C. Yang, "Gradientless Reactors and Transient Methods in Heterogeneous Catalysis," *Chem. Eng. Sci.* (to be published).
Boudart, M., "Kinetics of Chemical Processes," Prentice Hall, Englewood Cliffs, N. J. (1968).
Brandon, D. M., M.S. thesis, Univ. Conn., Storrs (1969).
Marquardt, D. W., "Solution of Nonlinear Chemical Engineering Models," *Chem. Eng. Progr.*, 55, 65 (1959).
Yang, C. C., M. B. Cutlip, and C. O. Bennett, "A Study of Nitrous Oxide Decomposition on Nickel Oxide by a Dynamic Method," in Proc. of 5th Intern. Congr. on Catalysis, Palm Beach, Fla. (to be published).
Yang, C. C., Ph.D. thesis, Univ. Conn., Storrs (1971).

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