# Kinetic Parameters for Coupled Bulk and Wall Reactions in a Tubular Flow Reactor

**Shih-Hsin Chang and**
**J. W. Bozzelli**
Department of Chemical Engineering
and Chemistry
New Jersey Institute of Technology
Newark, NJ 07102

When a species undergoes both wall and bulk (heterogeneous and homogeneous) reactions, it is difficult to determine their rate parameters simultaneously, although a simple relationship between these two parameters can be deduced under plug-flow conditions (Kaufman, 1961).

The appropriate continuity equation considering parabolic velocity profile, radial dispersion, bulk reaction, and wall reaction has been applied to kinetic studies of elementary reactions (Poirier and Carr, 1971; Smith et al., 1980). Lauwerier (1959) solved this laminar-flow model (excluding wall reaction). Wissler and Schechter (1961), using the solution of Lauwerier, carried out numerical calculations showing results in good agreement with those from the numerical method of Cleland and Wilhelm (1956). Black et al. (1974) took the wall reaction into account for deexcitation of nitrogen on a variety of different solid surfaces in their calculations, but their system excluded the bulk reaction.

There are two research studies which, in solving the governing continuity equation, considered both the bulk and the wall reactions. Poirier and Carr (1971) employed a finite-difference method to solve the continuity equation for first- and second-order chemical reactions, respectively. They displayed computer solutions of the continuity equation in graphical forms, which allowed convenient determination for kineticists. They did not, however, incorporate the two radial boundary conditions into the continuity equation when formulating their finite-difference equations (Lapidus, 1962); as a result, they underestimated the rate of species disappearance in the bulk reaction. The underestimate depends on the extent of the bulk reaction and is usually small for a fast-flow reactor, as employed in the work of Poirier and Carr and many similar studies. A second study, by Ogren (1975), solved the continuity equation in infinite series, but did not determine function coefficients using the boundary condition at the reactor entrance. Ogren then directed his work toward analysis of the deviation between a laminar-flow system and the plug-flow model. His results were significant, showing that the deviation depends on the dimensionless wall reaction rate variable $\beta$.

The bulk and wall reactions proceed in parallel, and the rate constants for these parallel reactions are coupled (Levenspiel, 1972). Poirier and Carr extracted the bulk rate constant $k_b$ from the overall (experimental) rate constant $k_{expt}$, using a previously known wall rate constant $k_w$, for the atomic hydrogen-nitrogen dioxide reaction system. Another study, by Smith et al. (1980), calculated $k_w$ for the heterogeneous recombination of oxygen atoms from the overall rate equation, with values of other kinetic parameters known. In the evaluation of one rate constant where the other is given, the known value may not always be applicable to the particular experimental conditions because the $k_{expt}$ value depends on the radius of the reactor used, as well as temperature, pressure, surface conditions, and reagent concentrations.

The purpose of this paper is to extend the analytical model of Lauwerier (1959) to include the wall reaction and to determine the true values of $k_b$ and $k_w$ simultaneously from their optimum values.

## Theory

The continuity equation considering parabolic velocity profile and radial dispersion for a species incurring both bulk and wall reactions is:

$$V_o[1 - (r/R)^2]\frac{\partial C}{\partial z} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) - k_b C \qquad (1)$$

with boundary conditions:

$$1.\ C = C_o \text{ at } z = 0 \qquad (2)$$

$$2.\ C = \text{ finite at } r = 0 \qquad (3)$$

$$3.\ -D_{AB}\frac{\partial C}{\partial r} = k_w C \text{ at } r = R \qquad (4)$$

The particular solution of Eq. 1 in its dimensionless form is (Chang, 1985; Lauwerier, 1959):

$$C(r, z) = \sum_{n=1}^{\infty} B_n \exp(-w_n z) \exp(-w_n^{1/2} r^2)\, {}_1F_1[a_n; 1; 2w_n^{1/2} r^2] \quad (5)$$

where

$$r = \frac{r}{R}, \quad z = \frac{4D_{AB}z}{V_o R^2}, \quad C = \frac{C}{C_o},$$

$$\text{and } a_n = \frac{1}{2} - \frac{w_n - \alpha}{2w_n^{1/2}}, \text{ with } \alpha = \frac{k_b R^2}{4D_{AB}}. \quad (6)$$

Determination of eigenvalue $w$ results from satisfying the boundary condition at $r = 1$, and requires solving Eq. 7 for its roots:

$$f(w) = (\beta - w^{1/2})\, {}_1F_1[a; 1; 2w^{1/2}] + 2aw^{1/2}\, {}_1F_1[a + 1; 2; 2w^{1/2}] \quad (7)$$

where

$$\beta = \frac{k_w R}{2D_{AB}}. \quad (8)$$

An analysis of Eq. 7 is helpful in the determination of eigenvalues; see Supplementary Material.

Determination of coefficient $B_n$ results from satisfying the boundary condition at $z = 0$, and yields the expression:

$$B_n = \frac{\int_0^1 r(1 - r^2) \exp(-w_n^{1/2} r^2)_1 \cdot F_1[a_n; 1; 2w_n^{1/2} r^2]\, dr}{\int_0^1 r(1 - r^2) \{\exp(-w_n^{1/2} r^2)_1 \cdot F_1[a_n; 1; 2w_n^{1/2} r^2]\}^2\, dr} \quad (9)$$

The response surface method (Box and et al., 1978) is employed to obtain optimum values of the kinetic parameters. The objective function is, of course, to minimize the sum of the squared residuals between experimental and calculated concentrations. The original rate constants, $k_b$ and $k_w$, rather than their corresponding dimensionless variables, $\alpha$ and $\beta$, are explicitly dealt with in the following treatment because the primary purpose of this work is to determine them. The optimization procedure results in an infinite number of pairs as optimum $k_b$ and $k_w$. This is because the bulk and wall reactions proceed in parallel, and infinite combinations of $k_b$ and $k_w$ are possible to produce the defined extent of reaction. On the response surface representing the sum of the squared residuals vs. ln $k_b$ and ln $k_w$, the pairs of optimum $k_b$ and $k_w$ form a smooth curve, from which the surface rises outward. The monotony of the surface allows easy evaluation of the optimum rate constants, while the curve makes determination of the true rate constants difficult.

The wall reaction rate is different from the bulk reaction rate and is based on a unit reactor surface. The wall reaction rates from reactors of different radius will be different if they are based on a unit reactor volume (because of different surface-to-volume ratios). This will generate different curves on the response surface for the optimum rate constants. Because the true rate constants are not functions of radius, they must locate at the intersection of the curves generated from different radii, as shown in Figure 1. The experimental reactors employed are usually small in radius and the use of different radius reactors will result in significantly different wall reaction rates when based on a unit reactor volume. The reactor radius $R$ can therefore be an effective decoupler to allow determination of $k_b$ and $k_w$.

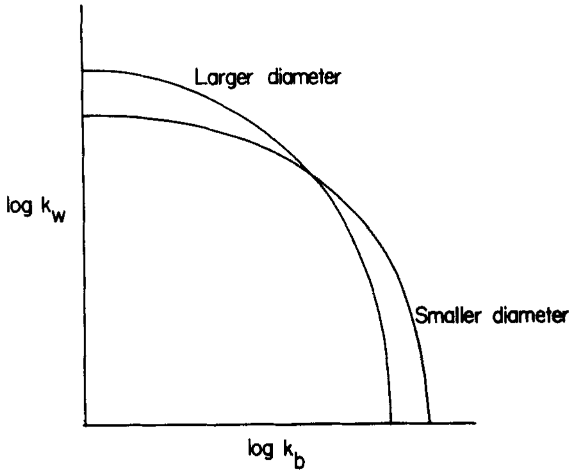

**Figure 1. Intersection of two curves characterized by diameter gives true values of log $k_b$ and log $k_w$.**

## Experimental Method

The experimental apparatus for the thermal decomposition of 1,1,1-trichloroethane (TCE) in a hydrogen environment has

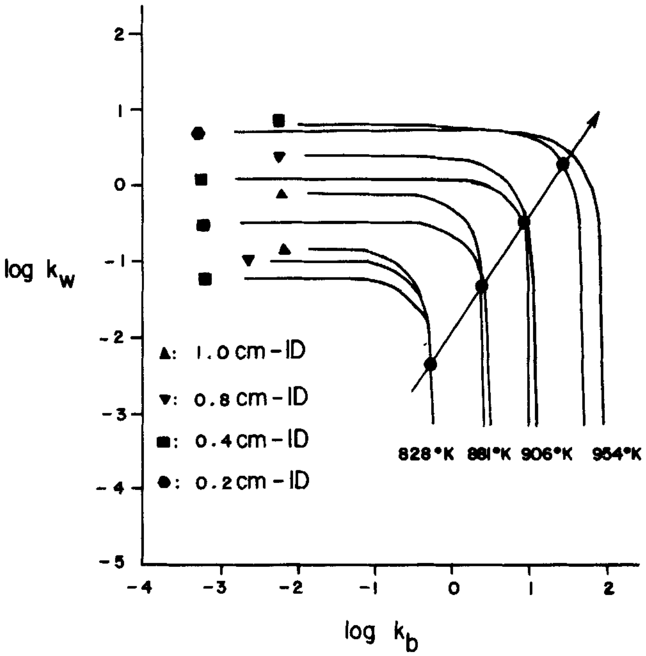

**Figure 2. $k_b$ and $k_w$ at 954 K are corrected by extrapolating the straight line of log $k_w$ − log $k_b$ to the 0.4 cm ID curve at 954 K.**

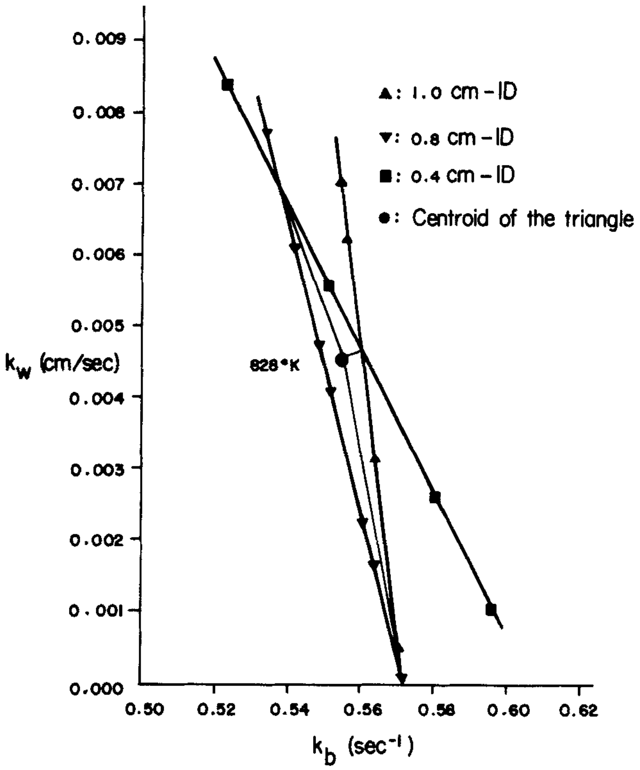

**Figure 3. Center of gravity of the triangle gives true values of $k_b$ and $k_w$.**

been described in detail by Mahmood (1985). Here a brief description is given. Hydrogen was bubbled through two series evaporators, where it became saturated with TCE at 278 K. The reactant mixture was then preheated (400°C) and entered the reactor. The reactor was 45 cm long and heated by a three-zone furnace to maintain an axially uniform temperature profile. The radial temperature gradient was assumed to be negligible because of small diameter. The products flowed through a glass wool filtering medium to trap possible carbon particulate and to destroy the laminar-flow pattern. The sample was analyzed by an on-line gas chromatograph and product identification was verified by a GC/MS.

Two different reactor diameters are required as a minimum to determine the specific rate constants $k_b$ and $k_w$. The diameters of reactors ranged from 0.2 to 1.0 cm and were determined by the extent of reaction and flow volume permitted by the system. The gas velocities ranged from 45 to 1,200 cm/s. The operating pressure was 1.05 atm. Four temperatures were run, 828, 881, 906, and 954 K, where kinetic data over a significant range of conversion were obtainable.

## Results

The major products from the thermal decomposition of TCE in hydrogen were 1,1-dichloroethylene and hydrogen chloride, suggesting that TCE was primarily decomposed via a cyclic, four-center transition state, yielding the above unimolecular decomposition products (Benson, 1976). The minor products over the temperature ranges studied included 1,1-dichloroethane, trichloethylene, chloroform, and methyl chloride. The disappearance rate of TCE was determined with varied reactor radii.

The results of optimization and decoupling are shown in Figure 2. Figure 3 shows that the centroid of intersections gives the true values of $k_b$ and $k_w$ when the intersections do not coincide.

Table 1 shows the dependencies of $k_b$ and $k_w$ on temperature. The wall reaction of TCE exhibits more than twice the activation energy of the bulk reaction. The corrected values of activation energies between the bulk and wall reactions still have a significant difference, as discussed below.

## Discussion

Kaufman (1961) showed that

$$V_o \frac{dC}{dz} = -k_{expt}C = -\left(k_b + \frac{2}{R}k_w\right)C \qquad (10)$$

when concentration is uniform or nearly so in the radial direction. Table 2 summarizes $k_{expt}$ values. The $k_b$ and $k_w$ values by Eq. 10 (the plug-flow model) were consistent with those from Eq. 1 (the laminar-flow model), as shown in Table 1. Table 3 shows that the validity of Eq. 10 for a laminar-flow reactor depends on $\alpha$, $\beta$ and $z$, which is consistent with the results of Walker (1961).

The decomposition reaction was vigorous at 954 K and some carbon deposit was found. A 0.2 cm ID reactor operating at higher space velocity was used to reduce the extent of reaction. The temperature profile in this reactor was not measured because the protected head of the thermocouple was comparable with its diameter. The 0.2 cm ID reactor was instead assumed to have the same temperature as that in the 0.4 cm ID reactor. The

**Table 1. Comparison of $k_b$ and $k_w$ from Laminar- and Plug-Flow Models**

| Temp. K | $k_b$, s$^{-1}$ Laminar | $k_b$, s$^{-1}$ Plug | $k_w$, cm/s Laminar | $k_w$, cm/s Plug |
|---|---|---|---|---|
| 828 | 0.561 | 0.537 | 0.0045 | 0.0057 |
| 881 | 2.66 | 2.17 | 0.0570 | 0.107 |
| 906 | 9.15 | 8.70 | 0.281 | 0.340 |
| 954 | 9.97[30.1]* | 11.2[30.7] | 4.47[1.86] | 3.87[1.85] |
| $E$, cal/mol | 38,200[50,600] | 40,200[51,600] | 85,900[76,000] | 80,800[72,500] |
| $A$, s$^{-1}$ | 8.04(9)**[1.23(13)] | 2.46(10)[1.99(13)] | 1.68(20)[5.01(17)] | 1.19(19)[8.87(16)] |

*Numbers in brackets are corrected values

**Numbers in parentheses indicate powers of ten

**Table 2. $k_{expt}$ ($s^{-1}$) Calculated Using the Plug-Flow Model**

| Temp. K | Radius, cm<br>0.1 | <br>0.2 | <br>0.4 | <br>0.5 |
|---|---|---|---|---|
| 828 | — | 0.605 | 0.572 | 0.571 |
| 881 | — | 3.23 | — | 2.59 |
| 906 | — | 12.1 | 10.4 | — |
| 954 | 87.5 [67.3]* | 48.8 | — | — |

Corrected value

$k_b$ and $k_w$ values obtained were determined to need correction. The correction on these $k_b$ and $k_w$ was made by fitting the rate constants measured at lower temperatures with the Arrhenius equation, as shown in Figure 2. The intersection of this straight line with the 0.4 cm ID curve gives the corrected $k_b$ and $k_w$ values, which are 30.1 $s^{-1}$ and 1.86 cm/s, respectively, as shown in Table 1. The corrected dependencies of $k_b$ and $k_w$ on temperature are shown in Figure 4, and the corrected rate equations are

$$k_b = 1.23 \times 10^{13} \exp(-25{,}500/T)\ s^{-1} \pm 13\% \qquad (11)$$

$$k_w = 5.01 \times 10^{17} \exp(-38{,}200/T)\ s^{-1} \pm 13\% \qquad (12)$$

The corrected value of $k_{expt}$ in the 0.2 cm ID reactor at 954 K is 67.3 $s^{-1}$, as shown in Table 2. The corrected $k_b$ and $k_w$ are accordingly 30.7 $s^{-1}$ and 1.85 cm/s, respectively (Table 1).

A parameter, such as the reactor radius $R$, which alters the ratio of the wall reaction rate to the bulk reaction rate may serve as an effective decoupler to separate $k_b$ and $k_w$. The wall reaction rate depends on radial diffusion, Eq. 4, and may be more easily retarded than the bulk reaction rate; see the supplementary material. Differences in radial diffusion may also change the ratio of the wall reaction rate to the bulk reaction rate. Diffusion coefficient $D_{AB}$ can therefore be a second parameter to decouple $k_b$ and $k_w$. It is however not practical to choose $D_{AB}$ as the decoupler because $D_{AB}$ only weakly affects the reaction rates (Carr and Poirier, 1971). A large difference in $D_{AB}$ would be needed to make two curves of the optimum rate constants significantly different in order to determine the true $k_b$ and $k_w$. Moreover, at least one $D_{AB}$ would have to be small (resulting from a high operating pressure) in order that the curves could be distinguishable. This would in addition make axial dispersion important and it would need to be included in the governing equation.

**Table 3. Criteria for Deviation of Laminar- from Plug-Flow Model**

| Criteria for 5% Deviation | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $z$ | 0.1 | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10 | 25 |
| $\alpha$ max* | 4.40 | 2.51 | 1.30 | 0.833 | 0.566 | 0.347 | 0.236 | 0.151 |
| $\beta$ max** | 1.19 | 0.727 | 0.397 | 0.261 | 0.178 | 0.108 | 0.0762 | 0.0467 |
| Criteria for 20% Deviation | | | | | | | | |
| $z$ | 0.1 | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10 | 25 |
| $\alpha$ max* | 6.42 | 3.64 | 1.85 | 1.19 | 0.800 | 0.485 | 0.339 | 0.212 |
| $\beta$ max** | 1.81 | 1.08 | 0.573 | 0.371 | 0.248 | 0.150 | 0.104 | 0.0647 |

% deviation = $(C_{laminar} - C_{plug})/C_{plug} \times 100\%$, where $C_{laminar}$ is the cup mixing concentration.

*with $\beta = 0$.

**with $\alpha = 0$.

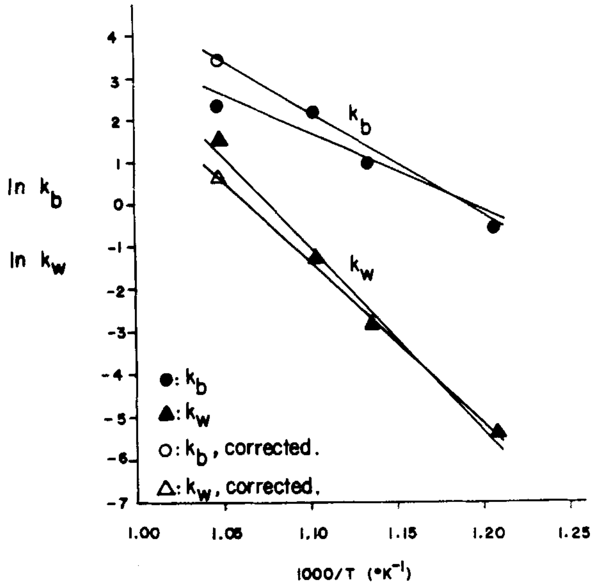

Fig. 4: Dependencies of rate constants on temperature.

The advantage of $R$ as the decoupler over $D_{AB}$ can also be seen from the entries of $R$ and $D$ into $\alpha$, $\beta$ and $z$. $D_{AB}$ appears in each dimensionless variable with the same order, while $R$ comes into the variables in different orders, i.e., $R^2$ in $\alpha$ and $z$, and only $R$ in $\beta$.

This method of determining the rate constants is also expected to be applicable when the reactions considered are other than first order because it has nothing to do with reaction orders. Either analytical or numerical solution of a continuity equation, such as Eq. 1, however, involves heavy computational work. It is recommended that one determine—for example, by matching the results from Eqs. 1 and 10—the conditions under which the plug-flow assumption is valid, and then operate the reactors under such conditions.

## Acknowledgment

The authors gratefully acknowledge support of this research through Grant No. 81R001401 of the United States Environmental Protection Agency.

## Notation

$a = (1/2) - (w - \alpha/2w^{1/2})$
$(a)_t = a(a+1)(a+2)\ldots(a+t-2)(a+t-1)$
$B_n$ = function coefficient
$C = C(r, z)$ = point concentration of species, mol/cm$^3$
$\mathbf{C} = \mathbf{C}(\mathbf{r}, \mathbf{z}) = C/C_o$ = normalized point concentration
$C_o$ = concentration of species at reactor inlet, mol/cm$^3$
$D_{AB}$ = diffusion coefficient of an $A - B$ binary system, cm$^2$/s
${}_1F_1[a; b; x] = \Sigma_{t=0}^{\infty} (a)_t x^t/(b)_t t!$
$f(w)$ = eigenvalue equation
$k_b$ = bulk rate constant, s$^{-1}$
$k_{expt}$ = experimental (apparent) rate constant, s$^{-1}$
$k_w$ = wall rate constant, cm/s
$R$ = radius of reactor, cm
$r$ = radial distance in reactor, cm
$\mathbf{r} = r/R$
$V_o$ = fluid velocity along central line of reactor, cm/s
$w_n$ = $n$th eigenvalue
$z$ = axial distance in reactor, cm
$\mathbf{z} = 4D_{AB}z/V_oR^2$
$\alpha = k_bR^2/4D_{AB}$
$\beta = k_wR/2D_{AB}$

## *Literature cited*

Benson, S. W., *Thermochemical Kinetics*, 2nd. ed., Wiley, New York, Ch. 3 (1976).

Black, G., H. Wise, S. Schechter, and R. L. Sharplwss, "Measurements of Vibrationally Excited Molecules by Raman Scattering. II: Surface Deactivation of Vibrationally Exited $N_2$," *J. Chem. Phys.*, **60**(9), 3526 (1974).

Box, G. E. P., W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley, New York, Ch. 15 (1978).

Chang, S. H., "Kinetic Modeling of a Laminar-Flow Reactor," Ph.D. Thesis, New Jersey Inst. Tech., Newark (1985).

Cleland, F. A., and R. H. Wilhelm, "Diffusion and Reaction in Viscous Flow Tubular Reactor," *AIChE J.*, **2**, 489 (1956).

Kaufman, F., "Reactions of Oxygen Atoms," *Progress in Reaction Kinetics*, G. Porter, ed., Pergamon, New York (1961).

Lapidus, L., *Digital Computation for Chemical Engineers*, McGraw-Hill, New York, Ch. 4 (1962).

Lauwerier, H. A., "A Diffusion Problem with Chemical Reaction," *Appl. Sci. Res.*, **A8**, 366 (1959).

Levenspiel, O., *Chemical Reaction Engineering*, 2nd. ed., Wiley, New York, Ch. 3 (1972).

Mahmood, B., "Reactions of Hydrogen with Chloroform and Trichloroethylene," M.S. Thesis, New Jersey Inst. Tech., Newark (1985).

Ogren, P. J., "Analytical Results for First-Order Kinetics in Flow Tube Reactors with Wall Reactions," *J. Phys. Chem.*, **79**(17), 1749 (1975).

Poirier, R. W., and R. J. Carr, "The Use of Tubular Flow Reactors for Kinetic Studies Over Extended Pressure Ranges," *J. Phys. Chem.*, **75**(10), 1593 (1971).

Smith, G. K., B. B. Krieger, and P. M. Herzog, "Experimental and Analytical Study of Wall Reaction and Transport Effects in Fast Reaction Systems," *AICHE J.*, **26**(4), 567 (1980).

Walker, R. E., "Chemical Reaction and Diffusion in a Catalytic Reactor," *Phys. Fluid*, **4**(10), 1211 (1961).

Wissler, E. H., and R. S. Schechter, "A Further Note on a Diffusion Problem with Chemical Reaction," *Appl. Sci. Res.*, **A10**, 198 (1961).

*Manuscript received Dec. 23, 1985, and revision received Sept. 22, 1986.*

See NAPS document no. 04510 for 5 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each of 10 pages of material thereafter, $1.50 for microfiche postage.