Experimental and Analytical Study of Wall Reaction and Transport Effects in Fast Reaction Systems

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This paper extends previous modeling calculations of concentration profiles and reaction rates in tubular flow reactors by including very fast wall reactions such as surface catalyzed atom recombinations. The plug flow assumption is investigated and found to be valid in tubular flow reactors when the dimensionless wall reaction rate is less than one ($H < 1$), and the dimensionless ratio of homogeneous reaction rate to diffusion rate (Damkohler number) is greater than one ($\alpha > 1$). If these criteria are not met, this work provides a correlation yielding a correction factor which can be applied to the mean residence time. The method is applied to experimental data relating to the deactivation probability of two types of atoms on teflon and quartz. Values of $1.0 + 0.2 \times 10^{-4}$ and $1.7+0.4\times10^{-4}$ for the deactivation probabilities of 0 and N atoms, respectively, are reported.

SCOPE

Recent advances in the understanding and modeling of complex reaction systems such as the atmosphere and combustion systems have been due, in large part, to the availability of reliable rate coefficients for fast free radical reactions. Many of these rate constants have been obtained in the laboratory using low pressure flow tube reactors in which the effects of transport processes are assumed to be negligible. However, some of these assumptions may contribute significantly to the error associated with measured rate constants. The objectives of this paper are to point out some of the errors made in these studies by not including consideration of the transport effects. We also point out the nature of the boundary condition (wall reaction) that may affect the concentration profile and thus the measurement of the apparent homogeneous rate constant.

Many previous investigators have used the plug flow assumption to determine species residence times (Kaufman, 1961) which, under certain conditions, represents a valid assumption. An analysis of this problem by Poirier and Carr pointed out the necessity of solving the continuity equation to determine experimental conditions where the plug flow assumption is valid. We will extend their analysis to include a range of boundary conditions (wall reaction rates) that are important in systems such as tube wall catalytic reactors and in the deactivation of very reactive species at vessel walls. The approach here will be to provide experimentalists with an empirical correction factor which can be applied to the residence time obtained using the plug flow assumption. This factor will account for the radial concentration profile, and hence nonuniform residence times, that can exist under many types of experimental conditions. The paper will also discuss the errors involved when a species concentration is detected in the radial direction by an integrating or averaging technique which may not take into account the substantial concentration gradients that exist. The concepts presented here are applied to the analysis of surface recombination rates for two atomic species found in combustion systems and the atmosphere.

CONCLUSIONS AND SIGNIFICANCE

July,

Owing to the current interest in energetic, rapid gas phase reactions important in the upper atmosphere, combustion systems and lasers, highly reactive species are being added to the long list of chemical compounds for which detailed rate constants are necessary. Many chemical kinetic studies in which these rate constants are measured have neglected the effects of transport processes, which become increasingly important as reaction rates become more rapid. A finite rate of wall deactivation for these very reactive species and a radial concentration profile giving rise to a distribution of residence times are two phenomena involving transport that have been overlooked as contributing to errors in studies of fast reactions. To aid in determining appropriate experimental conditions for studying these reactions, the regimes in which the plug flow assumption can be made have been reinvestigated to include the effects of fast wall reactions. These criteria are summarized in Table 1.

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When the plug flow assumption is valid, a convenient method for calculating the true heterogeneous rate constant has been presented. We stress the difference between the apparent rate constant determined from the axial concentration profile (k_d, units of frequency) and the true heterogeneous rate constant (k_w, units dependent on the boundary condition but most often units of velocity). The quantity k_d is often incorrectly reported as k_w in the chemical literature. For very reactive species, the quantity k_w has a strong effect on the radial concentration profile and can cause the average axial concentration detected to be in error depending upon the detection method.

The criteria developed here were applied to experiments involving reactions of N and O atoms. A true wall reaction rate constant k_w and the probability of molecular deactivation, γ were obtained for N and O atoms, γ being approximately 10^{-4} to 10^{-3} for both species on teflon and quartz.

When the plug flow assumption is not valid, we have presented a correlation that allows for the calculation of the representative residence time based on a knowledge of the homogeneous and heterogeneous rate constants and the diffusion coefficients for the species of interest.

Errors arising from the manner in which an optical detection device samples concentration in the radial direction are also analyzed. A model containing important geometrical considerations is included to point the way to obtain correct radially averaged concentrations when the radial concentration profile is nonuniform.

The kinetics of fast gas phase reactions involving free radicals and excited species are being studied in fast flow reactors to increase our knowledge of upper atmospheric phenomena, combustion systems and chemical laser systems. Tube-wall reactors show promise for carrying out highly exothermic, heterogeneously catalyzed, gas phase reactions, since the placement of the catalyst on the wall allows for better temperature control. For determining reaction rates in these systems, two important factors, the rapid wall reaction rate and the mass transfer by radial diffusion, can influence the measurement of rate constants by influencing the shape of the concentration profile. An additional factor is the bias of the concentration sampling technique and how sensitive it is to the shape of the concentration profile. This paper will address the problem of measuring concentrations and residence times when wall reactions are rapid and the concentration sampling technique measures the average concentration over a small axial distance along a diameter of a cylindrical reactor. This situation is frequently encountered in flow tube experiments (Krieger and Kummler, 1977; Smith, 1978), sidelight laser experiments (Lightman and Fisher, 1978) and some catalyst and combustion systems (Halpern and Rosner, 1978).

When a radially uniform concentration C_0 of a trace gas species is introduced into a cylinder with laminar flow and negligible wall reaction, the concentration profile can become parabolic, giving rise to a radial distribution of residence times across the reactor. In constrast, when the pressure is low, and hence diffusion rapid, radial transport may be fast enough to maintain a flat radial concentration profile against the laminar velocity profile. However, if rapid wall reaction occurs, large concentration gradients can be produced in spite of rapid diffusion. This latter effect can be particularly important when excited states or free radicals are present. Several studies (Cleland and Wilhelm, 1956; Walker, 1961; Kaufman, 1961; Poirier and Carr, 1971; Ahumada, 1974; Black et al., 1974; Ogren, 1975; Frisbee and Millikan, 1975; Davis, 1977) have attempted to determine under what combination of conditions (homogeneous and heterogeneous reaction rates, pressure, velocity, etc.) the residence time of a species in the reactor can be considered equal to the length of the reaction zone divided by an average velocity associated with the flow, that is, the plug flow assumption. An accurate value of the residence time is especially critical in obtaining experimental rate constants in a flowing system at low pressure, since the maximum velocity in laminar flow is twice the average velocity. Additional error may be introduced by measuring what is thought to be a uniform radial concentration with a measuring technique that may introduce sampling bias as a function of distance. This is true of some optical detection methods.

Walker addresses the question of the effect of heterogeneous reaction on the concentration profile by comparing an analytic solution to the continuity equation for the case of plug flow, with an approximate solution to the continuity equation for laminar flow. His laminar flow solution is valid only when z/R, the dimensionless axial distance, is large and $v_{avg}\, R/D_{AB}$ is near zero. Under these limiting conditions, Walker suggests that if Rk_w/D_{AB}, a dimensionless wall reaction rate, is less than 0.1, then the plug flow solution is within 5% of the approximate result. This criterion has been widely used in flow tube studies to justify the assumption that the residence time of all species in a reactor is the length of the tube divided by the average velocity.

Poirier and Carr, in an extensive treatment, use finite-difference techniques to integrate the continuity equation which included convection, radial diffusion, first-or second-order homogeneous reaction and heterogeneous wall reaction. Their results, when applied to a hydroxyl radical reaction set, qualitatively show that the assumption of plug flow can lead to rate constants which are smaller than the true rate constant. They also suggest that, in practice, a single parameter D_{AB}/k_1R^2, the ratio of diffusion rate to homogeneous reaction rate, can be used to evaluate the validity of the plug flow assumption. However, since this parameter does not include the effects of heterogeneous wall reaction, it will be shown that its use can lead to serious errors for the cases of interest in this paper.

Two other publications present series solutions to the continuity equation for the case of radial diffusion, first-order homogeneous reaction and heterogeneous reaction. Ogren defines a parameter G which represents the relative fractional difference between ideal (plug) and nonideal (laminar) flow in terms of the separation constant associated with the exponential decay portion of the solution. G values can be obtained from a knowledge of wall rate constants and binary diffusion coefficients. In an extension of an earlier work by Black et al., Frisbee and Millikan also obtain a solution to the aforementioned continuity equation. They present a method by which the wall rate coefficient can be extracted from the slope of an intensity or number density vs. normalized distance plot. This is an important contribution to the understanding of the dynamics of a flow tube reactor. However, Frisbee and Millikan and Ogren have failed to address the

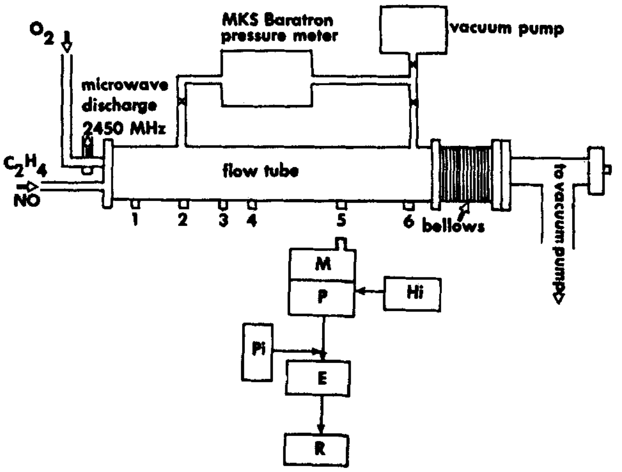

Figure 1. Schematic of the discharge flow tube apparatus and detection apparatus. M = monochromator Jarrell-Ash, P = photomultiplier, RCA C31034A (cooled), Hi = high voltage power supply, Pi = picoampere source, used with electrometer, E = Electrometer Keithley 602, or Canberra Photon Counting Electronics, R = recorder.

question of the effect of concentration profiles on residence time and the subsequent effects on experimentally determined rate constants.

The results cited previously are useful in many cases encountered in flowing systems. However, some conditions which are quite common have not been previously discussed. If the system of interest is operated at low pressures (less than about 1 torr which is an important regime for observing excited states), and if species are present which can react readily with the wall, large radial concentration gradients can occur. This effect is especially important in an experimental apparatus which detects the concentration along a diameter by optically integrating the emission from an excited species. Increased use of this technique is occurring owing to the high sensitivity this method affords for measurement of transient species present in low concentration in the atmosphere and in flames.

This work will examine the coupled processes of transport, reaction and detection via finite-difference integration of the continuity equation with Poiseuille flow. A simple method of determining effective residence times of the species in question, based on experimental conditions, will be presented. Also, conditions under which the plug flow assumption is valid will be examined. Of particular interest is the effect of rapid wall reaction on a concentration measurement made along a diameter. The weighting function an optical system (radially viewing aperture) can impose on a concentration measurement will be examined. Experimental measurements of N and O atom loss at the walls will be presented to validate the analysis.

EXPERIMENTAL APPARATUS

A steady state discharge flow tube consisting of a 4 cm diameter by 70 cm long stainless steel tube with radially viewing quartz windows was used in the measurement of O atom wall loss processes (see Figure 1; details appear in Krieger, 1975, and Smith, 1977). A teflon sleeve could be inserted to change the wall reaction rate. Pressure measurements were made with an MKS 77H Baratron capacitance manometer with pressure taps upstream and downstream of the reaction zone. Typical pressure drops in argon were about 10% at 1 torr total pressure.

A high gas velocity was typically about 50 m/s in argon and 100 m/s in helium. In order to ensure a uniform wall condition (MacKenzie et al., 1973), between experiments the reactor was maintained at 1 mtorr or less pressure.

Gas concentrations were continuously measured by their partial pressures. High purity gases were used from the manufacturer without further purification. Atomic species were created by a pulsed or continuous Raytheon Microwave discharge *PGM* 10 × 1 (2 450 *MHz*) driving a quarter-wave Evenson cavity. The gas to be dissociated flowed through the cavity in a quartz tube and was introduced into the reactor via a movable inlet tube with a spraylike teflon end. Nitrogen and oxygen atom concentrations were measured using NO and NO_2 titrations, respectively (Fontijn et al., 1973). Reactant gases were introduced via Hoke microvalves or flowmeters into a flowing stream of argon or helium which was then introduced into the reactor. Reactants were mixed several tube diameters upstream of the first viewing port to prevent observation of end effects. Absolute rate and concentrations were determined from the reaction chemiluminescence and chemical actinometry as described in Fontijn et al. (1964) and subsequent publications.

A photon counting detection system was employed to measure the radiation from excited species at several reaction times. The wave length dispersion was provided by a quarter-meter monochromator with 50 to 500 μ slits centered over the window perpendicular to the flow. A thermoelectrically cooled photomultiplier tube with sensitivity from 2 000 to 9 000 Å measured the chemiluminescence. Pulse counting of the PM tube output was accomplished, and an instantaneous rate meter provided an analog signal to a chart recorder. A phase sensitive lock-in amplifier with a cooled PbS infrared detector was available to monitor infrared chemiluminescence.

A second, similar apparatus was used to obtain some results reported here (Herzog, 1977). However, this system was made of quartz, the tube diameter was 1.53 cm ID and the velocity was about 10 to 20 m/s. The use of both systems provided a range of conditions under which the analysis could be tested.

Residence time (velocity) measurements were made electronically by observing the time delay in a pulse of emitting species at successive downstream distances. The signal was triggered by the pulsed microwave discharge reference frequency (Kennealy, 1970; Malki, 1972; Krieger, 1975; Smith, 1977). A discussion of this appears below.

VELOCITY CALIBRATION

The calculation of the average velocity from the viscous pressure drop has been discussed by many authors (Bird et al., 1960; Kaufman, 1967). However, for light emitting species, an additional method was used in these studies. Since the emitting species were created by reactions involving a pulsed source of atoms, they traveled in discrete packets in the flow tube and presented an oscillating signal to the emission detecting device. If the oscillating signal, measured at a downstream position, was compared to the reference signal (microwave discharge in Figure 1), a time delay was observed. If the time delay was measured at two different downstream positions, the velocity of the species observed was the distance between the two positions divided by the difference in time delay for each measurement. Discharge frequencies near 40 Hz with low duty cycle were chosen to maintain the integrity of the pulse. A more precise method involved the phase sensitive lock-in amplifier. The phase angle of the reference signal and the emission signal were recorded at two observation ports in the flow tube. The difference in phase angle divided by the frequency of the oscillation gave the time needed to travel the distance between the ports. Thus, the velocity of the emitting species was observed directly. The velocity measured using the NO + O emission was adopted as a standard plug flow velocity for this system according to the criteria set forth in this paper. The velocity of other emitting species :OH ($v = 1$)) was also measured directly (Krieger, 1975; Smith, 1977).

MATHEMATICAL MODEL

The steady state, constant density continuity equation with first-order homogeneous chemical reaction, parabolic velocity profile (Reynolds number, Re ~0.1 to ~35 in this system) and radial diffusion was used to model the concentration profile in a flow tube reactor. For conditions of this work, axial diffusion terms can be eliminated (Schneider, 1958; Levenspiel, 1972). With the assumption of isentropic flow and for pressure drops of less than 20% of the total pressure, the density is only weakly dependent on axial position in the measurement region and is assumed to be constant.

The continuity equation describing the concentration of a trace species in a diluent is

$$v(r)\frac{\partial c}{\partial z} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right] - R(c) \tag{1}$$

If the velocity v is independent of r (denoted as v_0), and the reaction rate $R(c)$ is the first order ($= k_1 c$), then Equation (1) can be solved by separation of variables. Two publications (Frisbee and Millikan, 1975; Ogren, 1975) have obtained series solution with recursive coefficients to Equation (1) using a parabolic velocity profile. However, only under limiting conditions of large downstream distances can these solutions be quickly approximated, making their use by experimentalists somewhat less likely.

The following development will review and compare the results of approximate solutions to Equation (1) for several cases of interest in fast flow systems to results obtained using the finite-difference solution technique. Insight into the physical processes occurring in low pressure flow systems can be obtained in this fashion, and a comparison can be made between analytic predictions and experimental results.

Plug Flow With Wall Reaction

For plug flow and $R(c) = k_1 c$ (first-order homogeneous reactions), the analytical solution gives insight into the apparent axial decay of a species due to radial diffusion and homogeneous reaction loss. In dimensionless form, Equation (1) becomes

$$\frac{\partial C}{\partial \lambda} = \alpha\left[\frac{1}{\zeta}\frac{\partial C}{\partial \zeta}\left(\zeta\frac{\partial C}{\partial \zeta}\right)\right] - C \tag{2}$$

where

$$\lambda = k_1 z/v, \quad \zeta = r/R, \quad C = c/c_0, \text{ and } \alpha = D_{AB}/k_1 R^2$$

for plug flow. Appropriate boundary and initial conditions for the case of first-order heterogeneous wall reactions are

$$dc/dr = 0 \quad \text{at} \quad r = 0 \quad \text{for all} \quad z$$

$$c = c_0 \quad \text{at} \quad z = 0 \quad \text{for all} \quad r$$

and

$$-D_{AB}\, dc/dr = k_w c \quad \text{at} \quad r = R \tag{3}$$

The familiar solution (Carslaw and Jaeger, 1959; Churchill, 1969) is given by the infinite series

$$C = \sum_n A_n J_0(\phi_n \zeta) \quad \exp \quad (-b_n^2 \lambda) \tag{4}$$

where

$$A_n = 2H/[J_0(\phi_n \zeta) + (\phi_n^2 + H)] \tag{5}$$

$$H = Rk_w/D_{AB} \tag{6}$$

$$\phi_n^2 = (b_n^2 - 1)/\alpha \tag{7}$$

$$\phi_n J_1(\phi_n) = H J_0(\phi_n) \tag{8}$$

Equation (8) is the solution to the derivative boundary condition at the wall, and its roots are tabulated for various values of H (the dimensionless wall reaction rate constant) by Carslaw and Jaeger. Some useful insight into the physical aspects of the problem can be gained from further examination of the analytic solution.

Since the experimentalist usually only measures the axial concentration profile implied by the axial derivative of C on the left-hand side of Equation 2, we would like to rewrite only the radial derivatives in Equation (2) in terms of the solution, Equation (4). Taking the radial derivative $dC/d\zeta$ of Equation (4) and substituting in Equation (2), we obtain

$$\frac{\partial C}{\partial \lambda} = -\alpha \sum_n {\phi_n}^2 A_n \exp(-{b_n}^2 \lambda) J_0(\phi_n \zeta) - C \tag{9}$$

Inspection of the roots of Equation (8) shows that the first root, ϕ_1, is large so that only the first term in the sum of Equation (9) need be considered (see, for example, Carslaw and Jaeger). This approximation fails under conditions where $H > 100$ and $\alpha < 0.01$, corresponding to simultaneous extremely fast wall and homogeneous reaction. This is a small fraction of the systems of interest. Removing ϕ_n^2 from the sum, we can rewrite (9) as

$$\frac{\partial C}{\partial \lambda} = -\alpha \phi_1^2 C - C \tag{10}$$

or, in dimensional form

$$v\frac{\partial c}{\partial z} = -\frac{D_{AB}}{R^2}\phi_1^2 c - k_1 c \tag{11}$$

where $-D_{AB}\phi_1^2 c/R^2$ represents the loss of c through radial diffusion and subsequent wall reaction at a rate embodied in ϕ_1^2. If we let

$$D_{AB}\phi_1^2/R^2 = k_d \tag{12}$$

with units of seconds^{-1}, then Equation (11) can be written in the conventional kinetic form

$$dc/dt = -(k_d + k_1)c \tag{13}$$

where, in the reactor, $t = z/v_{avg}$. Thus we see the axial decay of concentration as the sum of two effects, the wall and homogeneous loss, and this can result in over estimation of k_1 for improperly designed experiments. We stress this point and note that k_d is a strong function of total

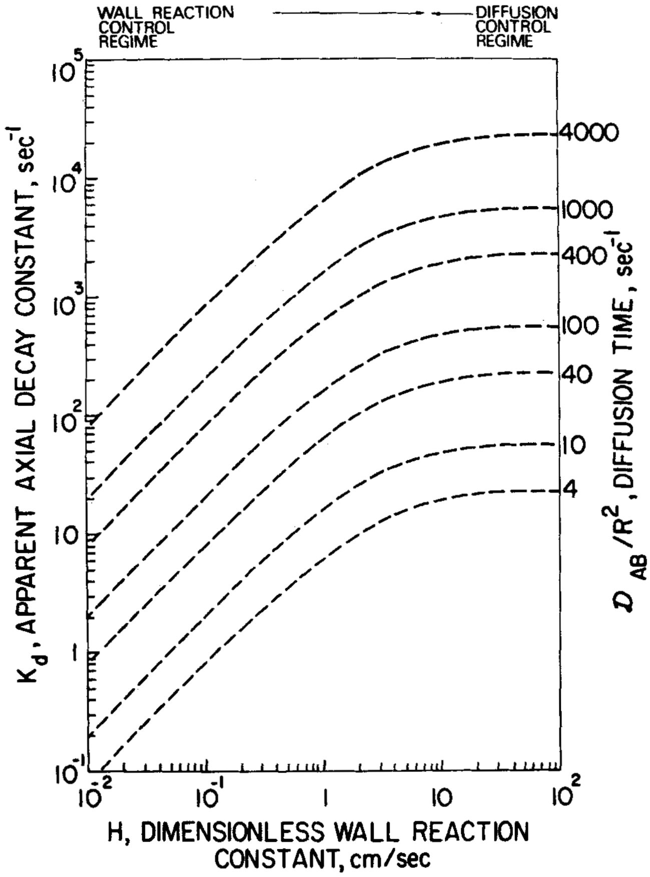

Figure 2. Apparent axial decay constant (k_d) as a function of dimensionless wall reaction rate H and diffusion rate D_{AB}/R^2 calculated using plug flow assumption.

pressure and diluent as well as the heterogeneous rate constant, k_w. This is shown graphically in Figure 2, where, in the right portion, the extremes of very fast wall reaction ($H > 10$) have little or no effect on k_d; only the diffusion rate (expressed as D_{AB}/R^2) *affects* k_d. On the other hand, when $H < 1$, k_d is strongly (exponentially) dependent on both the diffusion rate D_{AB}/R^2 and H, the wall rate parameter.

Under conditions of plug flow and small k_1 (the homogeneous first-order loss reaction coefficient) compared to k_d, Equation (13) can be used to obtain k_d from the slope of concentration vs. time measurements. If we know the tube radius and the diffusion coefficient, ϕ_1 can be obtained from the definition of k_d, Equation (12). From Carslaw and Jaeger, a value of $H = Rk_w/D_{AB}$ can be found as a function of ϕ_1 which leads directly to k_w once D_{AB} has been estimated.

In many investigations, wall reaction rate constants are reported as pseudo first-order rate coefficients k_d, with units of seconds^{-1}, and not as true heterogeneous rate coefficients k_w, in units of centimeters/seconds. The quantity k_w depends on fundamental molecular parameters such as the mean molecular speed of the gas species and the deactivation probability γ at the specific surface (Black et al., 1974; de Boer, 1968; Kaufman, 1961). Definitions of the quantity k_w and the boundary conditions in gas-solid reactions vary owing to differences in problem approach. The problems addressed generally fall into four categories:

1. The wall is considered an infinitely fast reacting surface in an otherwise homogeneous reaction system. Here the radial loss is governed by the rate of diffusion

2. The wall is considered a sink for the otherwise homogeneously reacting system, and the boundary condition of Equation (3) applies when the mass balance is done on the gas. In this case we assume a finite rate of first-order loss reaction of a gas species at the surface and say nothing about the wall reaction products. The rate constant k_w is related to molecular parameters through kinetic theory governing collisions of molecules with a stationary surface (de Boer, 1968).

3. The surface or wall is considered an integral part of the reacting system in which we are concerned about not only transport to the surface from the homogeneous phase, but also the mechanism and products of reaction at the surface, such as in a tube wall reactor with a catalyst on the wall. We then may employ the models of Rideal or Langmuir-Hinshelwood to incorporate finite rates of adsorption, reaction and desorption as well as the possiblity of higher-order concentration dependence of the surface reaction. The focus here is actually on the surface rather than the homogeneous kinetics.

4. The surface is dispersed throughout the reacting gas (or liquid) phase, as when reactive compounds of smog are scavenged by atmospheric aerosols. A surface area comparable to or greater than the vessel walls is present. If the rates of homogeneous and heterogeneous loss of reactant are comparable, we may wish to choose an approach such as Judekis and Siegel (1973) did, who essentially treat the surface as a homogeneous species with an area per unit volume. Thus, the surface loss appears not as a boundary condition but as a homogeneous loss term in the continuity equation (Easley, 1979).

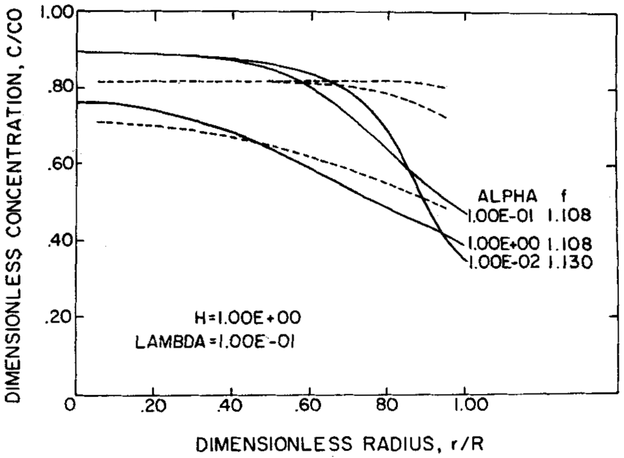

Figure 3. Dimensionless concentration vs. dimensionless radius for the cases of plug flow (- - - - - -) and Poiseuille flow (————) wall reaction (H = 1.0) and homogeneous reaction (α = 1, 0.1, 0.01) are included in both cases.

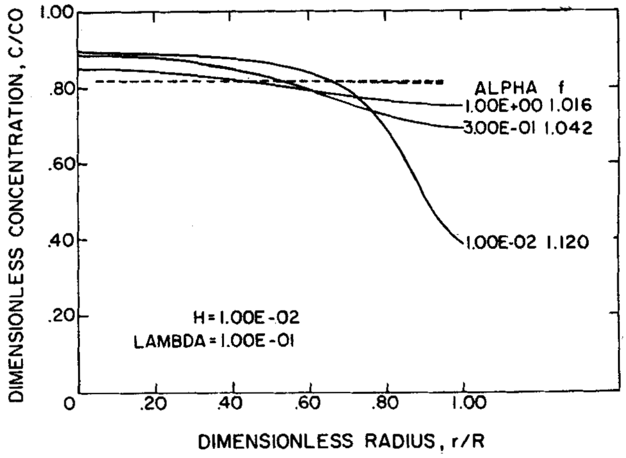

Figure 4. Dimensionless concentration vs. dimensionless radius for the cases of plug flow and Poiseuille flow. Wall reaction (H = 0.01) and homogeneous reaction are included for both cases.

Poiseuille Flow With Wall Reaction

Concentration profiles were obtained through a numerical solution of Equation (1) when the plug flow velocity was replaced with a laminar velocity profile as described in Poirier and Carr (1971). Typical results are shown in Figures 3 and 4, where Poiseuille concentration profiles (solid lines) are contrasted with those for plug flow (dashed lines) calculated from the infinite series solution in Equation (4) for several values of the dimensionless parameters. Figure 3 may be the concentration profile for a typical vibrationally excited species that experiences both a rapid wall loss reaction and a rapid homogeneous loss reaction. Figure 4 shows concentration profiles for species undergoing slower homogeneous and heterogeneous reaction rates typical of N and O atoms. Concentration profiles for other conditions appear in Krieger (1975) and Smith (1977). Of particular interest to the kineticist is the actual residence time of the species of interest. Often one can assume that the correct residence time is an observation distance divided by the average velocity in laminar flow; that is, the plug flow assumption holds. As the system deviates from plug flow and the wall reaction rate becomes substantial, the reactant concentration near the wall becomes depleted with respect to the concentration at the center line. As a result of detecting concentrations along a diameter with an optical method, the measurement is weighted towards the center line, where the species velocity can be twice the average velocity.

Previously, Poirier and Carr and Walker have suggested qualitative criteria for determining the validity of the plug flow assumption. Table 1 summarizes the criteria.

TABLE 1. SUGGESTED CRITERIA FOR VALIDITY OF THE PLUG FLOW ASSUMPTION

	Dimensionless wall reaction rate H	Dimensionless homogeneous loss rate α	Dimensionless axial distance λ
Walker	<0.1	Weak dependence	Independent
Poirier and Carr	Independent	>0.5	Independent
This work	<1	>1	Independent

Both previous papers indicated that λ, the dimensionless axial distance, had little effect on the validity of this assumption. Walker suggests that values of H less than 0.1 will limit errors in the concentration profile to less than 5%, while Poirier and Carr indicate H has little bearing on the results. As shown in Figures 3 and 4, the effect of H on the concentration profiles can be substantial. Walker, on the other hand, states that α does not strongly influence the bounds for the one dimensionality of the problem. It appears that Walker's restrictions of large dimensionless axial distance, $z/R >> 0$, and the range of α he used ($0.1 < \alpha < 100$), caused his solutions to show only a weak dependence on α. Poirier and Carr have not addressed the problem of studying highly reactive species at the wall by only investigating small values of H. When H is small, the rate of diffusion (α) can be smaller and still give a flat concentration profile. Results of this work differ somewhat from both these authors. We suggest for $\alpha > 1$ and $H < 1$, the plug flow concentration agrees with the Poiseuille flow concentration. This applies for all values of dimensionless axial distance as also indicated by the previous authors.

For many purposes, the values of $H < 1$ and $\alpha > 1$ will be sufficient to determine the validity of the plug flow assumption. However, for the case of fast wall reaction ($H = Rk_w/D_{AB} > 1$, possible with excited states), and/or slow diffusion ($\alpha = D_{AB}/k_1R^2 < 1$), an accurate estimate of the possible error of the residence time associated with the plug flow assumption is needed. In this case, the residence time can be determined by the velocity of the average concentration which is defined as

$$<v>_c = \int C(r)v(r)rdr \Big/ \int C(r)rdr \qquad (14)$$

where $C(r)$ is the concentration profile and $v(r) = v(\max) *(1-r^2/R^2)$ is the parabolic velocity profile. Two possible cases arise: $C(r) =$ constant, or $C(r) =$ function of r. If $C(r) =$ constant, the integral in Equation (14) reduces to

$$v(c) = v(\max)* \int \qquad {}^{2}/R^2)rdr \Big/ \int rdr = v(\text{avg}) \qquad (15)$$

which indicates that if the concentration profile is flat, then the velocity of the average concentration is equal to the average velocity. If the concentration profile is a function of r, then we have the following form of Equation (14) which, when written in dimensionless form and slightly rearranged, gives

$$<v>_c = v(\text{avg})* \left[2 \int C(x)(1-x^2)xdx / \int C(x)xdx \right] \qquad (16)$$

where $x = r/R$. If the expression in brackets is defined as f, Equation (16) can be written as

$$<v>_c = v(\text{avg})*f \qquad (17)$$

The f factor is then a correction to the residence time implied by the average velocity and can be calculated if $C(r)$, the concentration profile, is known.

The concentration profiles for a large number of these parameters in the ranges

$$\begin{gathered} 0.01 < H < 10. \\ 0.1 < \lambda < 1.1 \\ 0.01 < \alpha < 2.0 \end{gathered} \qquad (18)$$

were calculated numerically from the continuity equation with Poiseuille flow (Krieger, 1975; Smith, 1977). From this, f was calculated using Equation (16). These values of f were fit to an equation of the form

$$f = A(H)^B(\alpha)^C \qquad (19)$$

using the least-squares technique. The values for the constants are as follows:

$$A = 1.0872$$

$$B = 0.01194$$

$$C = -0.0402$$

The average error of the fit was 4.5%, with the minimum error being 1.2% and the maximum 18%. There was no correlation between any parameter and the magnitude of the error. As demonstrated by this work and that of previous workers, the value of λ has little bearing on the plug flow assumption. Values of f are shown in Figures 3 and 4. As an example, using Figure 4, for $H = 0.01$ and $\alpha = 0.1$, the velocity of the average concentration is 1.12 times the average velocity. As H becomes large, this deviation, represented by f, increases.

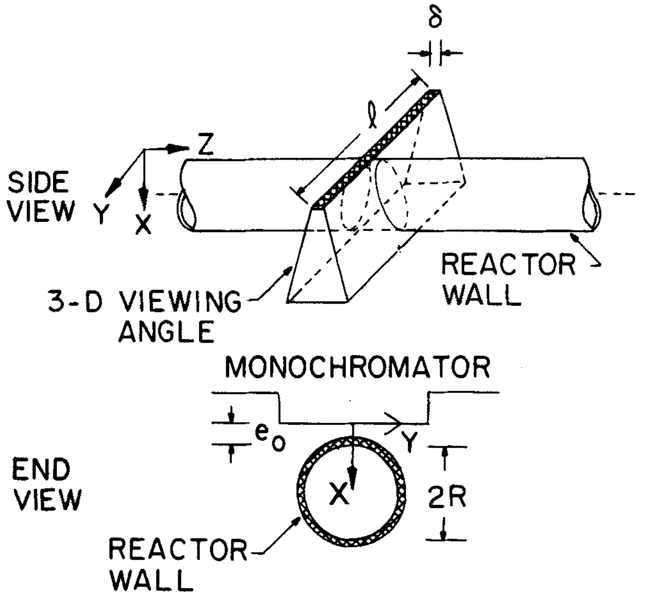

Figure 5. Geometry of the sampling technique using a radially viewing F4 monochromator on a cylindrical flow tube reactor.

Concentration Measurement Errors With Radial Sampling

The foregoing analysis is valid when one can accurately measure the concentration of interest at a given axial distance. The technique used must either sample the average concentration or correctly account for any sampling bias when the measurement is averaged along the radial concentration profile as in optical spectroscopic methods. In one measurement technique, the radiation intensity (proportional to concentration) is observed along a tube diameter through a monochromator viewing angle determined by the slit width as shown in Figure 5. The decay of detector sensitivity (as $1/x^2$) and the radial concentration profile can cause the measured intensity to be weighted in such a way that the concentration near the center line of the reactor (traveling with a velocity twice v_{avg} in laminar flow) contributes a greater fraction to the measured intensity. A method to account for this bias is given below.

The integrated dimensionless intensity at the viewing slit (cross hatched rectangle of length l and width, δ, in Figure 5) is given in rectangular coordinates as

$$\frac{I_{\text{total}}}{2} = \frac{1}{R^3}\int_{y=0}^{y=\sqrt{R^2-(x-R-e_0)^2}} dy \int_{e_0}^{e_0+2R} dx \int_{-\left[\delta+\frac{1}{4}x\right]}^{\left[\delta+\frac{1}{4}x\right]} I^*(x,y)F(x,y,z)\,dz \qquad (20)$$

The factor one-half comes from the fact that symmetry in the y dimension allows one half the solid angle to be treated; the factor $1/R^3$ makes the integral dimensionless. The following quantities are defined:

$I^*(x) =$ reduced intensity at a given axial distance, $z = 0$ proportional to the dimensionless concentration of radiating species; made dimensionless by multiplying by $(I_{\max})^{-1}$, the intensity at $r = 0$; assumed constant over z.

$F(x,y,z) =$ inverse square law governing radiation intensity decay with distance from a source; $= \left(\frac{e_0^2}{x^2+y^2+z^2}\right)$ (e_0 appears so that all arbitrary intensities will be relative to the intensity at $x = e_0$). (21)

$\delta + \frac{1}{4}x =$ triangular slit function, $F4$ viewing, $\delta =$ slit width which is generally very small (typically 150 μm.) (22)

$e_0 =$ distance from slit to inside reactor wall.

The upper limit on y is either the radius of the reactor (presented here) or related to the slit function, $y = l/2 + 1/4x$, depending on the dimensions of the reactor and slit.

The integral can be solved numerically using concentration profiles such as those appearing in Figures 3 and 4, but for purpose of illustration, a parabolic concentration

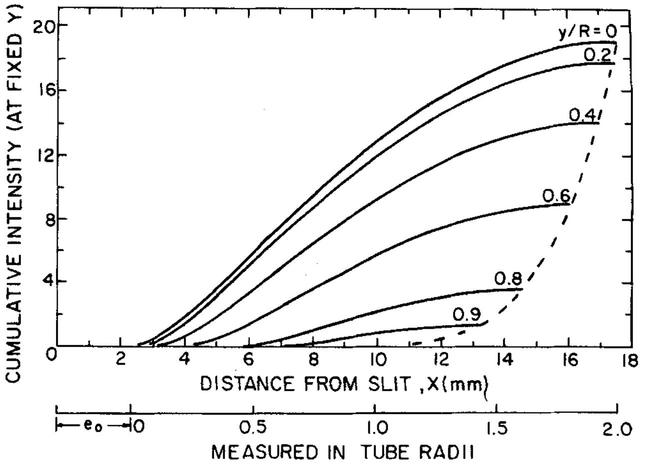

Figure 6. Contributions to the cumulative intensity integrated in the x dimension. Each curve represents the incremental contribution to the overall observation from a measurement using longer slits in the y dimension.

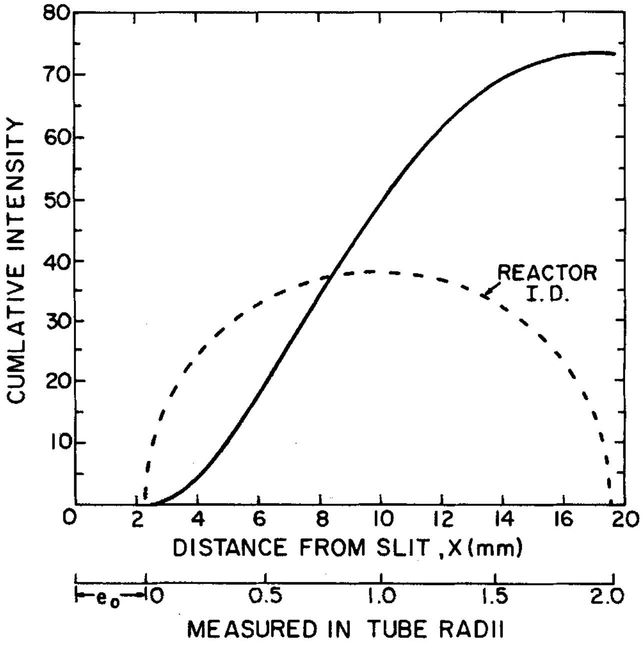

Figure 7. Total integrated intensity as a function of distance from the detector slit (integrated over the slit length) observed by the sampling technique using a parabolic concentration profile.

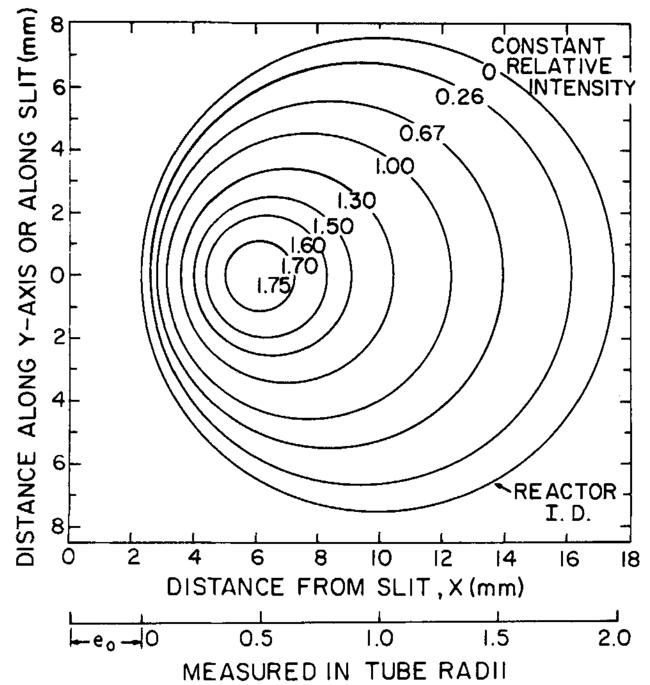

Figure 8. Calculated lines of constant apparent intensity viewed by the detector.

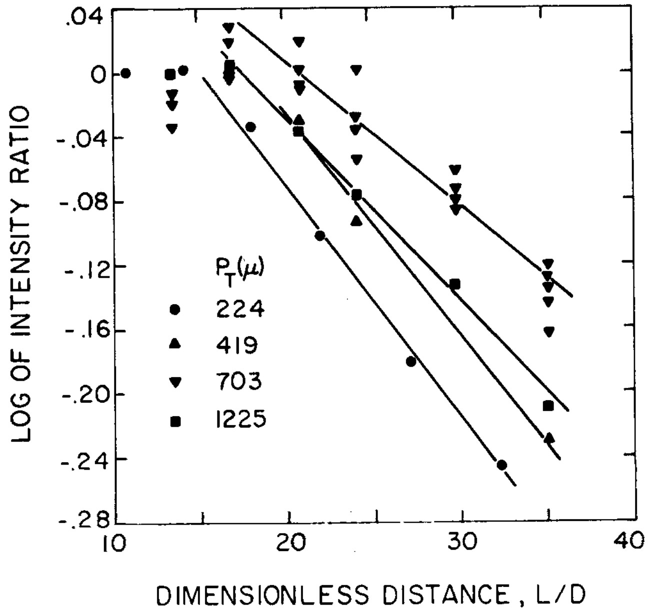

Figure 9. Log of intensity ratio of the *NO* + O reaction vs. dimensionless distance for several total pressures.

profile was chosen with a steeper gradient than shown in Figure 3. After integrating in the x and z directions at fixed y, one obtains the cumulative intensities as a function of x as shown in Figure 6. Qualitatively, this figure points to the fact that increasing the length of the slit beyond about $y/R \simeq 0.6$ will result in small contributions to the total intensity due to the parabolic nature of the concentration profile; that is, the central portion of the reactor contributes most of the intensity viewed by a monochromator.

Integrating over x, y, and z results in cumulative intensity plotted vs. the distance from the slit to the far wall of the reactor, Figure 7. Since this is a cumulative intensity plot, one can subtract the integrated intensities at two values of x to get the intensity coming from that annular portion of the reactor. The figure shows that 80% of the total intensity seen by the monochromator is the result of emissions from only 60% of the reactor. As the wall reactor thickness or the observation distance e_0 is made larger, this error increases. To further clarify this phenomenon, Figure 8 shows lines of constant apparent intensity for the chosen parabolic concentration profile. We see that the maximum intensity is not at the center of the reactor. For this case, the velocity at the apparent maximum intensity is 0.73 times the maximum velocity, while the average velocity is 0.50 times the maximum. This means that the volume element that is contributing most to the signal is traveling at 1.46 times the average velocity. Thus the actual rate constants for this case are also 1.46 times those calculated using the average velocity.

The experimentalist should be cautioned that these results apply to the concentration profile used here, $I^*(x,y)$, and that the assessment for the particular reactions of interest should be made using Equation (20) and the appropriate concentration profile.

EXPERIMENTAL RESULTS: Rate Constants for Wall Deactivation of O and N Atoms

As an application of the foregoing analysis, we consider the heterogeneous recombination of O and N atoms on the walls of the previously described apparatus. The atomic species were generated in a microwave discharge under experimental conditions such that the plug flow assumption was valid, that is, $H < 1$ and $\alpha > 1$. The oxygen atom concentration was inferred by measuring the emission from excited NO_2 (NO_2^*) which was formed by the NO + O reaction system. The reactions important in describing the O atom loss process and the NO_2^* emission are shown below:

		Reference
$O + NO \xrightarrow{1} NO_2^*$	$k_1 = 6.4 \text{ to } 11.4 \times 10^{-17} cm^3/s$	Stair, 1967; Fontijn et al., 1964; Vanpee et al., 1971; Golde et al., 1973
$NO_2^* \xrightarrow{2} NO_2 + h\nu$	$k_2 \sim 10^6 s^{-1}$	
$O + NO + M \xrightarrow{3} NO_2 + M$	$k_3 = 7.4 \times 10^{-32} cm^6/s$ $M = N_2$	NBS-CIAP, 1975
$O + NO_2 \xrightarrow{4} NO + O_2$	$k_4 = 6.9 \times 10^{-12} cm^3/s$	NBS-CIAP, 1975
$O + O_2 + M \xrightarrow{5} O_3 + M$	$k_5 = 6.6 \times 10^{-34} cm^6/s$	NBS-CIAP, 1975
$O\vert_{wall} \longrightarrow \text{products}$	$k_d = s^{-1}$	

where k_d is the apparent axial decay. We can assume constant O_2 and M, and essentially constant NO_2 and NO, (Fontijn, 1973; Herzog, 1977), giving in the steady state

$$[NO_2^*] = \frac{k_1[NO]\,[O]}{k_2} \tag{23}$$

and

$$[NO_2] = \frac{k_3\,[O]\,[NO]\,[M] + k_2[NO_2^*]}{k_4\,[O]} \tag{24}$$

Thus the O atom loss is described by

$$-\frac{d[O]}{dt} = k_1\,[NO]\,[O] +$$

$$k_3\,[NO]\,[M] + k_4\,[O]\,[NO_2] + k_5\,[O]\,[O_2]\,[M] + k_d\,[O] \tag{25}$$

TABLE 2. REPRESENTATIVE CALCULATIONS OF WALL DEACTIVATION COEFFICIENT FOR O ATOMS

Experimental conditions	Run #1	Run #5	Run #7	Run #9
P_1 (in Torr), upstream pressure	0.224	0.419	0.703	1.225
v (cm/s)	450	820	1 130	1 430
$[O_2]$ (molec/cm^3)	4.12×10^{15}	8.3×10^{15}	1.62×10^{16}	3.22×10^{16}
[NO] (molec/cm^3)	1.12×10^{15}	1.52×10^{15}	1.09×10^{15}	1.65×10^{15}
k_d (s^{-1})	4.1 ± 0.7	6.5 ± 0.9	7 ± 1	9.93 ± .09
γ	1.0×10^{-4}	1.6×10^{-4}	1.7×10^{-4}	2.4×10^{-4}

Average value $\gamma = 1.7 \times 10^{-4}$

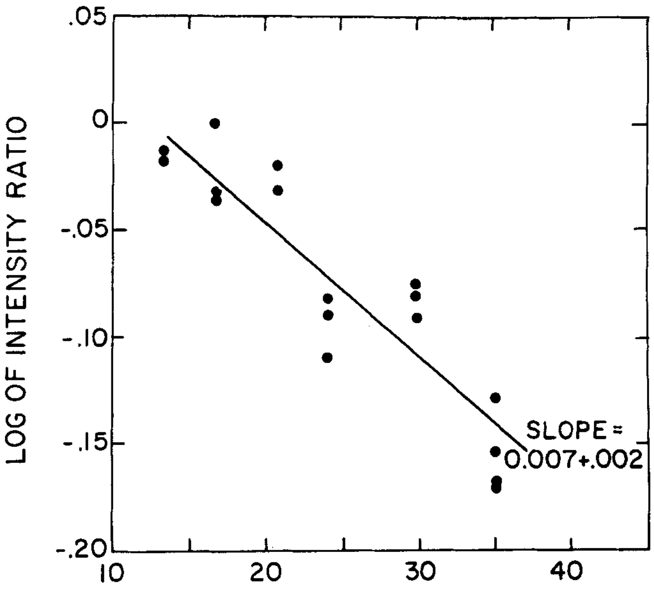

Figure 10. Log of intensity ratio of the nitrogen recombination afterglow vs. dimensionless distance.

for data that have been corrected for pressure drop. Substituting (23) in (24) and the result in (25), we get

$$-\frac{d[O]}{dt} = 2k_1[NO][O] + 2k_3[M][NO][O] + k_5[O][O_2][M] + k_d[O] \quad (26)$$

Integration of (26) gives

$$\ln\frac{[O]}{[O]_0} = \{2k_1[NO] + 2k_3[M][NO] + k_5[M][O_2] + k_d\}\cdot t \quad (27)$$

From (23) it can be seen that the intensity of emission, $k_2[NO_2^*]$, is proportional to the O atom concentration, $I = k_1[NO][O]$. Since $k_1[NO]$ is a constant in this system (Fontijn et al., 1964), the fraction of original oxygen atoms $[O]/[O]_0$ is equal to the intensity ratio I/I_0. A plot of $\ln I/I_0$ vs. the time $t = z/v$ has a slope equal to the bracketed terms in Equation (27), where all the terms except k_d are known.

Intensity vs. distance data were obtained at four pressures and are presented in Figure 9. From the slope of these lines, it is verified that the homogeneous loss contributes about 10% to the loss of O atoms in this system. As outlined previously, k_w can be obtained from k_d and appears in Table 2. Note that k_d is dependent on pressure through D_{AB} and is not a constant as is often reported.

As outlined by Jablonski (1976) and Walker, Black and others, the wall deactivation coefficient γ can be determined from k_w. γ is the fraction of collisions with the wall that results in deactivation or reaction,

$$\gamma = \frac{4k_w}{v_{\text{molecular}}} \quad (28)$$

for low surface coverage. With assumptions as outlined by Frank-Kamenetski (1969) and de Boer, γ was calculated from the data and is shown inTable 2. The wall deactivation coefficient γ should not vary with pressure or velocity but should only be dependent on the species involved and the type of surface onto which the adsorption occurs. The average value of γ obtained for O deactivation on quartz, $\gamma = 1.7 \times 10^{-4}$, is larger than values of γ for silica and Pyrex glass reported by Kaufman but reasonable compared to the value reported by Judeikis and Wu for quartz with a barium oxide coating and is within the range of values reported for other oxide compounds (Black, 1974; Jablonski, 1976).

A similar analysis can be made for N atoms using the emission of N_2^* (B-A) formed by the homogeneous recombination of N atoms as a tracer for the atoms. Details are presented in Herzog (1977), where it is shown that a first-order expression describes the decay; that is

$$[N] = [N_0]e^{-k_d t} \quad (29)$$

for

$$[N_2] = 2\,090\mu = 6.9 \times 10^{16}\text{molecules/cm}^3$$

$$[N]_0 = 12\mu = 3.96 \times 10^{14}\text{molecules/cm}^3$$

Figure 10 shows a graph of the N_2^* intensity ratio plotted vs. L/D. From the slope we obtain

$$k_d = 4 \pm 1 s^{-1}$$

In a manner similar to that presented for O atom decay, we find k_w and

$$\gamma = 1.0 \pm 0.2 \times 10^{-4}$$

The only comparison value of γ for N atoms is on Pyrex, a different material.

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NOTATION

A_n = coefficients for Bessel function solutions
b_n = separation constant
C = dimensionless concentration, c/c_0
c = species concentration, molecules/cc
c_0 = initial species concentration at $z = o$
D_{AB} = binary diffusion coefficient, cm^2/sec
e_0 = wall reactor thickness plus distance of observation from reactor, cm
f = residence time correction factor
F = reverse square law factor reducing radiation intensity from a point source as a function of distance
H = Rk_w/D_{AB}, dimensionless wall reaction rate constant
I, I^* = arbitrary intensity of radiation from emitting species
J_0, J_1 = Bessel functions of the first kind
k_w = hetergeneous wall reaction rate constant, cm/sec
k_1 = homogeneous first order rate constant, sec^{-1}
k_d = apparent axial decay constant, sec^{-1}
$L/D = L/2R$ = dimensionless axial distance in experimental apparatus
R = tube radius, cm
$R(c)$ = homogeneous reaction loss rate, molecules/cc/sec
v_0 = plug flow velocity, cm/sec
v_{av} = average velocity in laminar flow, cm/sec.
$v(r)$ = axial velocity profile as a function of r
$<v>_c$ = velocity of the average concentration
$v_{molecular}$ = kinetic theory velocity of a molecule
z = axial distance, cm

Greek Letters

α = D_{AB}/k_1R^2, parameter measuring ratio of diffusion rate to homogeneous reaction rate, like a Damkohler Number.
γ = probability of surface deactivation of a species
δ = monochromator slit width
λ = k_1z/v = dimensionless axial distance
ϕ_n = root of boundary condition equation, a measure of wall reaction rate versus diffusion rate
ζ = r/R, dimensionless radius

LITERATURE CITED

Ahumada, J. J., and J. V. Michael, "Chemical Kinetic Effects of Walls on Active Species, Results for Hydrogen Atoms," *J. Phys. Chem.*, **78**, No. 5, 465 (1974).

Bird, R. B., A. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).

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

Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford, London, England (1959).

Churchill, R. V., *Fourier Series and Boundary Value Problems*, 2 ed., McGraw Hill, New York (1969).

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

Davis, C. C., and M. E. Lewittes, "The Interpretation of Relatation Rate Measurements Made in Flow Systems," *Int. J. Chemical Kinetics*, **IX**, 235-247 (1977).

deBoer, J. H., *The Dynamical Character of Adsorption*, Oxford, London, England (1968).

Easley, P., "Kinetics of Free Radical Scavenging by Aerosols," M.S. thesis, Univ. Washington, Seattle (1980).

Fontijn, A., C. B. Meyer, and H. T. Schiff, "Absolute Quantum Yield Measurements of the NO-O Reaction and Its Use as a Standard for Chemiluminescent Reactions," *J. Chem. Phys.*, **40**, 64 (1964).

Fontijn, A., D. Golomb, and J. A. Hodgeson, "A Review of Experimental Measurement Methods Based on Gas-Phase Chemiluminescence," *Chemiluminescence and Bioluminescence*, D. Lee Hercules and M.J. Cormier, ed., Plenum Press, New York (1973).

Frank-Kamenetskii, D. A., *Diffusion and Heat Transfer in Chemical Kinetics*, 2 ed., Plenum Press, New York (1969).

Frisbee, R. H., and R. C. Millikan, "Surface Deactivation of Excited Molecules in a Circular Cylinder with Diffusion, Convection, and First Order Chemical Reaction," *Chem. Phys. Lett.*, **36**, 23 (1975).

Golde, M. F., A. Roche, and F. Kaufman, "Absolute Rate Constant for the O+NO Chemiluminescence in the Near Infrared," *J. Chem. Phys.*, **59**, 3953 (1973).

Halpern, B., and D. E. Rosner, "Chemical Energy Accommodation at Catalyst Surfaces; Flow Reactor Studies of Association of Nitrogen Atoms on Metals at High Temperatures," *J. Chem. Soc. Faraday Trans.*, **I 74** (8), 1833-912 (1978).

Herzog, P. M., "The Effect of N Atoms and Vibrationally Excited N_2 on the Formation of NO in the N_2 and Molecular O_2 Systems," M.S. thesis, Univ. Washington, Seattle (1977).

Judeikis, H. S., and S. S. Siegel, "Particle Catalyzed Oxidation of Atmosphere Pollutants," *Atmos. Env.*, 7, 619 (1973).

Judeikis, H. S., and J. Wun, "Measurement of Chlorine Atom Diffusion," *J. Chem. Phys.*, **68**, 4123 (1978).

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

Kennealy, J. P., private communication (1970).

Krieger, B. B., M. M. Malki, and R. H. Kummler, "Chemiluminescent Reactions of Reactive Hydrocarbons and Atomic Oxygen," *Env. Sci. Technol.*, **6**, 742-744 (1972).

Krieger, B. B., Ph.D. thesis, Wayne State Univ., Detroit Mich. (1975).

———, and Kummler, R. H., "Mathematical Model and Experiments to determine the mechanism and rate constant of OH Chemiluminescence from Oxygen Atom Attack on Ethylene," *J. Phys. Chem.*, **81**, 2493 (1977).

Levenspiel, O., *Chemical Reaction Engineering*, Wiley, New York (1972).

Lightman, A. J., and E. R. Fisher, "CO Vibrational Distributions to High Levels in Low Pressure CO/He Mixtures," *J. Appl. Phys.* **49** (3, Pt.1), 971-5 (1978).

Malki, M. M., M.S. Thesis, Wayne State Univ., Detroit, Mich. (1972)

McKenzie, A., M. F. R. Mulcahy, and J. R. Steven, "Kinetics of Decay of Hydroxyl Radicals at Low Pressure," *J. Chem. Phys.*, **59**, 3244 (1973).

Mulcahy, M. F. R., and B. C. Young, "Heterogeneous Reactions of OH Radicals, Int. Symp. Chem. Kin. Proc. — Data for Upper and Lower Atmosphere," No. 1, 595 (1975*a*).

————————— "The Reaction of Hydroxyl Radicals with Carbon at 298° K," *Carbon*, **13**, 115 (1975*b*).

NBS-CIAP, R. F. Hampson, and D. Garvin, Eds., "Chemical Kinetics and Photochemical Data for Modeling Atmospheric Chemistry," *NBS Tech. Note*, **866** (1975).

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

Poirier, R. W., and R. J. Carr, "The Use of Tubular Flow Reactors for Kinetic Studies Over Extended Pressure Ranges," *ibid.*, **73**, 1593 (1971).

Rosner, D. E., and H. H. Feng, "Energy Transfer Effects of Excited Molecule Production by Surface-Catalyzed Atom Recombination," *J. Chem. Soc. Faraday Trans.*, **I** 884 (1970).

Schneider, P. J., "Effect of Axial Fluid Conduction on Heat Transfer on Entrance Regions of Parallel Plates and Tubes," Heat Transfer and Fluid Mechanics Institute, Stanford University Press (1956).

Senkan, S. M., L. B. Evans, and J. B. Howard, An Analysis of Tube Wall Reaction under Diffusion Limiting Conditions," *Ind. Eng. Chem. Process Design Develop.*, **15**, 184 (1976).

Smith, G. K., Ph.D. thesis, Wayne State Univ., Detroit, Mich. (1977).

Stair, A. T., Jr., and J. P. Kennealy, "Infrared Chemiluminescence and Vibraluminescence in the NO-O-O_2 Reaction System," *The Chem. Phys.*, **46**, 831 (1967).

Vanpee, M., K. D. Hill, and W. R. Kineyko, "Absolute Rate Constant Measurements for the Radiative Combination of Atomic Oxygen with Nitric Oxide," *AIAA Journal*, **9**, 135 (1971).

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

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